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Heat treatment of electrospun Polyvinylidene fluoride fibrous membrane separators for rechargeable lithium-ion batteries

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HIGHLIGHTS

- Heat treatment was introduced to improve the mechanical properties of electrospun PVDF fibrous membrane separators.
- Heat-treated PVDF fibrous membranes exhibit high electrochemical oxidation limit.
- Heat-treated PVDF fibrous membranes have low interfacial resistance with lithium electrode.
- Li/$LiFePO_4$ cells using heat-treated PVDF fibrous membranes show high charge/discharge capacities and good cycle performance.

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ABSTRACT

Polyvinylidene fluoride (PVDF) fibrous membranes for use as lithium-ion battery separators were prepared by electrospinning technique. Heat treatment was introduced to improve the tensile strength and elongation-at-break as well as the tensile modulus of PVDF fibrous membranes, with the best mechanical properties achieved after treatment at 160 °C for 2 h. After heat treatment at 160 °C for 2 h, the ionic conductivity of the liquid electrolyte-soaked PVDF fibrous membranes was 1.35×10^{-3} S cm^{-1} at room temperature. Moreover, compared with commercial Celgard 2400 separator, heat-treated PVDF fibrous membranes exhibited higher electrochemical stability window and lower interfacial resistance with lithium electrode. In addition, at a 0.2C rate, Li/$LiFePO_4$ cells using heat-treated PVDF fibrous membrane separator showed high charge/discharge capacities and stable cycle performance.

1. Introduction

Separator is a critical component in rechargeable lithium-ion batteries and it plays an important role in determining the battery performance [1–3]. The main function of a separator is to keep the positive and negative electrodes apart to prevent electrical short circuits while enabling free ionic transport [1–3]. Currently, most commercial separators are based on microporous membranes made from polyolefins such as polyethylene and polypropylene [4–6]. These polyolefin separators have good mechanical strength, suitable thickness, and excellent chemical stability [7–9]. However, they have several disadvantages including low porosity, unsatisfactory thermal stability, and poor wettability in liquid electrolytes [7–9]. These disadvantages cause high cell resistance and restrict the performance of lithium-ion batteries. As a result, to obtain high-performance lithium-ion batteries, alternative separators with excellent overall properties are needed.

In recent years, electrospinning has been widely used as a new method to prepare fibrous membranes for use as separators in lithium-ion batteries [10,11]. Electrospun fibrous membranes have high porosities, large specific surface areas and interconnected porous structures, and as a result, they are able to uptake large amounts of liquid electrolytes and offer effective conduction channels, which in turn lead to high ionic conductivities and good electrochemical properties [10,11]. Many polymers such as polyacrylonitrile (PAN), polyethylene oxide (PEO), polymethyl methacrylate (PMMA), polyvinylidene fluoride (PVDF) and polyvinyl alcohol (PVA), etc., have been used as the host polymer for the preparation of electrospun fibrous membranes as separators for

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lithium-ion batteries [12–16]. Among these polymers, PVDF has attractive significant attention because of its good thermal and electrochemical stabilities, and excellent affinity to electrolyte solutions [17,18]. Moreover, PVDF-based separators contain fluorine atoms and have excellent anodic stability and high dielectric constant ($\varepsilon = 8.6$), assisting the ionization of lithium salts [19–21]. However, the practical use of electrospun PVDF fibrous membranes is restricted by their insufficient mechanical properties. Electrospun PVDF fibrous membranes are inherently weak and cannot withstand the large tension developed by the winding operation during battery assembly [22].

In this study, heat treatment was used to improve the mechanical properties of electrospun PVDF fibrous membranes. It was found that heat treatment of PVDF fibrous membranes significantly improved their tensile strength and elongation-at-break as well as the tensile modulus. The influence of heat treatment on the morphology and electrochemical performance of PVDF fibrous membranes was also investigated. Results demonstrated that heat-treated PVDF fibrous membranes are promising separator candidate with improved mechanical properties and excellent electrochemical performance.

2. Experimental

2.1. Membrane preparation and heat treatment

Polyvinylidene fluoride (PVDF, MW = 400,000, Kynar 761) was purchased from Sinopharm Chemical Reagent Co., Ltd., and was vacuum dried at 60 °C for 12 h before use. N,N-Dimethylacetamide (DMAc) and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd., and they were used as received without further purification.

PVDF was dissolved in a mixed solvent of DMAc/acetone (7:3, V/V) to obtain a 12 wt.% solution, which was stirred for 12 h at 60 °C. During electrospinning, the solution was fed in a 10 ml syringe and delivered with a flow rate of 0.4 ml h^{-1} under applied voltage of 16 kV. The distance between the needle tip and the collector was 20 cm. The electrospun fibers were accumulated on the collector, forming free-standing fibrous membranes. The resultant PVDF fibrous membranes were then dried under vacuum at 60 °C for 12 h to remove the solvent residual before further use.

The heat treatment of PVDF fibrous membranes was carried out under vacuum, and the heat treatment conditions were shown in Table 1.

2.2. Structure characterization

The morphology of PVDF fibrous membranes before and after heat treatment was observed by scanning electron microscope (SEM, TM-1000, and Hitachi) with an accelerating voltage of 5 kV. The crystal structure variation of the PVDF fibrous membranes before and after heat treatment was identified by differential scanning calorimeter (DSC, PE7, Perkin–Elmer Co., U.S.A) with a heating rate of 10 °C min^{-1} over a temperature range of 50–200 °C under nitrogen atmosphere. The crystallinity was calculated based on:

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^*} \times 100\% \quad (1)$$

where ΔH_f is the measured melting enthalpy of PVDF fibrous membrane, and ΔH_f^* the melting enthalpy (104.7 J g^{-1}) of 100% crystalline PVDF. The wide-angle X-ray diffraction (WXRD, RIGAKU, Japan) was carried on a D/Max-2550 PC X-ray diffractometer recorded using CuKα radiation with an experimental condition of 45 kV and 50 mA, at a scanning rate of 2° min^{-1} and 2θ range of 5–90°.

The porosities of PVDF fibrous membranes were determined by soaking them in *n*-butanol for 2 h until equilibrium was achieved at room temperature. The excess *n*-butanol adhering to the membrane surface was gently removed with wipes. The porosity (*P*%) was calculated by:

$$P\% = \frac{W_w - W_d}{\rho_b \times V_m} \times 100\% \quad (2)$$

where W_w and W_d were the weights of the electrolyte-soaked membrane and dry membrane, respectively, ρ_b the density of *n*-butanol, and V_m the volume of the dry membrane.

2.3. Mechanical property tests

Tensile strengths, moduli and elongations-at-break of PVDF fibrous membranes were determined by an electronic tensile strength tester (XQ-2 Fiber Tensile Testing Machine, Shanghai, China). Measurements were carried out with a crosshead speed of 5 mm min^{-1} and gauge length of 30 mm. The reported values were the averages of at least five specimens for each sample.

2.4. Electrolyte uptake measurements

The liquid electrolyte uptakes of PVDF fibrous membranes were measured by soaking them in a liquid electrolyte of 1 mol L^{-1} $LiPF_6$–ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) for 4 h. The liquid electrolyte uptake was calculated based on:

$$EU = \frac{W_1 - W_0}{W_0} \times 100\% \quad (3)$$

where W_1 and W_0 were the weights of the electrolyte-soaked membrane and dry membrane, respectively.

2.5. Electrochemical performance evaluation

The ionic conductivities of liquid electrolyte-soaked PVDF fibrous membranes were measured by electrochemical impedance spectroscopy using a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Inc., China). The membranes were placed between two stainless steel blocking electrodes, and spectra were obtained by sweeping from 100 kHz to 0.1 Hz with an AC amplitude of 10 mV at room temperature. The ionic conductivity (σ) was calculated from the following equation:

$$\sigma = \frac{d}{R_b \times S} \quad (4)$$

where R_b is the bulk resistance, and *d* and *S* are the thickness and area of the fibrous membrane, respectively.

Table 1
Temperatures and times used for the heat treatment of PVDF fibrous membranes.

Sample no.	Heat treatment temperature (°C)	Heat treatment time (h)
A (Untreated)	–	–
B (Heat-treated at 150 °C)	150	2
C (Heat-treated at 155 °C)	155	2
D (Heat-treated at 160 °C)	160	2