THERMAL TREATMENT FOR NANOFIBROUS MEMBRANE

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Poly(vinylidene fluoride) nanofibrous membranes with high porosity, large electrolyte solution uptake, and adequate mechanical properties were prepared by electrospinning. The physical properties of the electrospun poly(vinylidene fluoride) membranes can be improved by thermal treatment. Results showed after the thermal treatment, there had appeared ever-increasing tensile strength and elongation of the poly(vinylidene fluoride) membranes. The crystal structures of poly(vinylidene fluoride) fibers were greatly improved.

Key words: *electrospinning, poly(vinylidene fluoride) membranes, thermal treatment, physical properties*

Introduction

In recent years, there has been a growing demand for high-energy density rechargeable lithium batteries for portable electronic products because of their advantages including safety, high-energy density, high single cell voltage, geometry, and no memory effect [1]. Poly(vinylidene fluoride) (PVDF) and its copolymer have been widely studied for applications in rechargeable batteries [2]. It has been reported that increasing the pore size in the PVDF matrix can help to enhance the ionic conductivity and thus improve cell rate capability. Polymer electrolytes have been obtained both by the standard casting procedure [3], and by the absorption/extraction method [4].

Electrospinning technology recently came into the spotlight for applications in fields such as filters, biomedical materials, fiber mats in reinforcing components, clothing providing protection from electromagnetic waves, sensor engineering, radioactive radiation, and electronic devices [5]. In this paper, a PVDF nanofibrous membrane was prepared by electrospinning. The membrane was thermally treated to improve the physical and mechanical property. The effect of thermal treatment on diameter and crystalline of electrospun PVDF fibers was researched.

Experiment

Poly(vinylidenefluoride) (PVDF) solutions were prepared with 15 wt.% by using mixture of N, N-dimethylformamide (DMF) and acetone with weight ratio 8:2. Electrospinning experiments were carried out with the same collective distance (15 cm), voltage applied (15 kV) and flow rate (1 ml/h) at the room temperature (25 ºC) and 55% relative humidity in a vertical spinning configuration. The electrospun nanofibrous membrane was thermally treated at 160 ºC for 2 hours.

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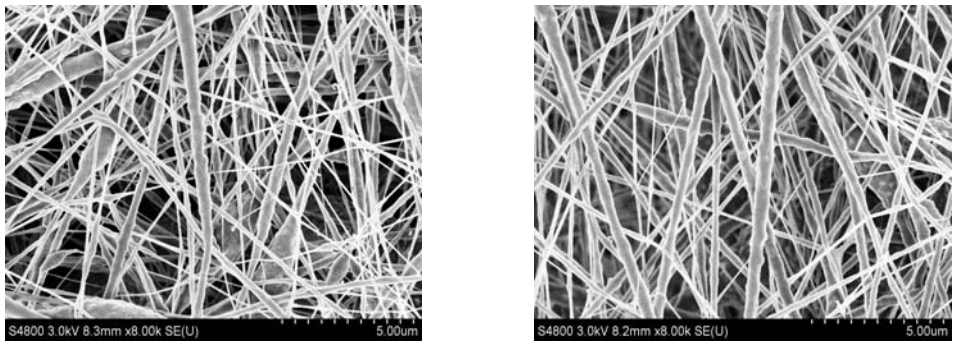
Results and discussion

Figure 1 showed SEM pictures of the electrospun PVDF membranes before and after thermal treatment. The results illustrated the average diameter of the untreated PVDF nanofibers was 188 nm, fig.1(a). The electrospun PVDF membranes after thermal treatment had more even distribution of nanofiber than the untreated PVDF membranes. But the average diameter of the thermally treated PVDF nanofibers is 194 nm, fig.1(b). This phenomenon was due to the fiber shrinkage occurred at elevated temperatures.



(a) before thermal treatment (b) after thermal treatment

Figure 1. SEM images and diameter distribution of PVDF fiber membranes before and after thermal treatment

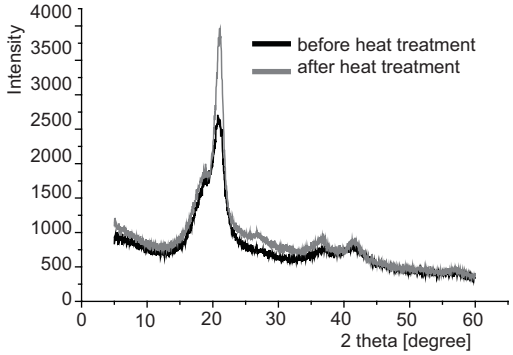


Figure 2. XRD patterns of PVDF nanofibrous membranes prepared before and after heat treatment

Table 1. Tensile properties of PVDF nanofibrous membranes

Temperature [°C]	Tensile strength [MPa]	Elongation [%]
25	3.49	15.4
160	8.92	27.5

The crystalline of the PVDF nanofibrous membranes was determined by an X-ray Diffractometer. The XRD patterns of PVDF nanofibers prepared before and after thermal treatment were shown in fig. 2. It illustrated the crystal peaks of PVDF nanofibrous membranes obtained by thermal treatment were sharpened which proved that the degree of crystallinity of the PVDF was obviously increased by thermal treatment.

Table 1 showed the tensile strength and elongation-at-break values of PVDF nanofibrous membranes before and after thermal treatment. It was seen that the tensile properties of PVDF nanofibers were improved by thermal treatment. The improvement in tensile properties for heat-treated PVDF fibrous membranes was the result of the increased fiber diameter, the formation of interfiber bonding, and the enhanced crystallinity [6].

The porosities of PVDF nanofibrous membranes were determined by soaking them in n-butanol for 2 hours 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 [7]:

Table 2. Porosities of the PVDF nanofibrous membranes

Temperature [°C]	Porosity [%]
25	83.6
160	80.0

$$P\% = \frac{W_w - W_d}{\rho_b V_m} 100\%$$

where W_w and W_d are 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.

The results of porosity measurements were presented in tab. 2. It was seen that the porosity of the PVDF nanofibrous membranes decreased slightly after thermal treatment. The decrease in membrane porosity was mainly caused by the increased fiber diameter after thermal treatment.

Conclusions

In order to improve the mechanical properties, the electrospun PVDF membranes were thermally treated at 160 °C for 2 hours. The tensile strength and elongation-at-break of the thermally treated PVDF membranes were higher than those of the untreated membranes. The improved physical properties were explained with the increased fiber diameter, the fiber shrinkage and the enhanced crystallinity. Although the porosity decreased after thermal treatment, the porosity (80.0%) achieved at 160 °C was still significantly higher than those of commercial separators. These results showed that the thermally treated PVDF membranes would be a promising separator candidate for lithium-ion batteries.

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