

Short communication

Preparation and characterization of new microporous stretched membrane for lithium rechargeable battery

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Abstract

The microporous membrane based on poly(vinylidene fluoride) (PVdF) is prepared with phase inversion method. In addition to phase inversion process, solvent pre-evaporation and uni-axial stretching processes were introduced to enhance tensile strength and ionic conductivity of the membrane.

The tensile strength of the membrane after 200% stretching was about 52 MPa, which is four times higher than that of the membrane without stretching. The ionic conductivity of the membrane soaked with liquid electrolyte was also increased from 6.1×10^{-5} to 8.6×10^{-4} S cm⁻¹ at room temperature by taking the stretching process.

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1. Introduction

The separator plays an important role in rechargeable lithium batteries since it can keep the positive and negative electrodes apart to prevent electrical short circuits. It can also transport ionic charge carriers that are needed to complete the circuit during the passage of current in an electronic chemical cell. There are many requirements for the high performance of the separator: electronic insulation, minimal electric resistance, sufficient tensile strength to allow easy handling, chemical resistance to degradation by electrolyte, and good wettability with electrolyte [1–3].

Poly(ethylene) (PE)-based separators have been generally used in conventional lithium secondary batteries. The PE separators have good mechanical properties and they can also effectively prevent thermal runaway that results from short-circuit of rapid overcharging of the battery. On the other hand, they exhibit poor compatibility with liquid electrolytes due to their hydrophobic property [4]. To enhance the affinity with liquid electrolytes, it may be necessary to consider more hydrophilic polymers as a separator in the lithium secondary batteries.

In this work, a separator which is a microporous membrane based on PVdF, is prepared by phase inversion method. PVdF is generally known to be more compatible with liquid electrolyte than the normal PE separators, however, it shows a poorer mechanical property. It is one of the most serious deficiencies that limit them from being used in practical cells [5,6].

In this work, we have studied on the enhancement of tensile strength and ionic conductivities of PVdF membranes. For higher tensile strength and ionic conductivities, we additionally introduced solvent pre-evaporation and uni-axial stretching processes for the membrane.

2. Experimental

2.1. Materials and membrane preparation

A homopolymer of PVdF (SOLEF6020: weight average molecular weight 320,000) provided by SOLVAY was dissolved in *N,N*-dimethylformamide (DMF, Aldrich). Polymer solutions were prepared by heating a mixture of PVdF and a solvent (1:4 in weight ratio) in a round bottom flask at 70 °C for 5 h. After complete dissolution, the solution was cast on a glass plate with doctor blade. The cast polymer films were solvent pre-evaporated in dry oven at 90 °C for 1–4 min and then immersed

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into coagulation bath filled with non-solvent (distilled water) to generate micro-pores. After 6 h, the membranes were washed with methanol and dried at room temperature to remove the residual solvent.

2.2. Scanning electron microscopy (SEM)

The specimens for the SEM images of the cross-section of the films were prepared by fracturing the films in liquid nitrogen. The SEM images of the polymer films were taken by using the JEOL 5360.

2.3. X-ray diffraction and thermal analysis

The prepared membranes were subjected to X-ray diffraction analysis using JEOL 8030 X-ray diffractometer with a nickel filtered Cu K α radiation. Thermal behaviors of the membranes were studied by using a differential scanning calorimeter (Dupont TA 2000 DSC). Each sample was loaded in hermetically sealed with aluminum pans and scanned at a heating rate of 10 °C min⁻¹ over a temperature range of -100 to 250 °C under nitrogen atmosphere.

2.4. Tensile strength

Tensile strength of the membrane was determined by using an Instron 5583 Tensile Tester. Polymer membrane was stretched uni-axially when the clamps move apart from each other at a constant rate of 10 mm min⁻¹. The exact stretch ratio was determined by dividing the final length of the stretched portion of film to its initial length before stretching. After releasing the film at ambient temperatures, about 5% length reduction of the stretched film was observed due to polymer elastic recovery.

2.5. Electrical measurements

The membranes immersed in liquid electrolyte (1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC)/propylene carbonate (PC)=30/65/5 by vol.%: Cheil Industries, Korea) were sandwiched between the two stainless-steel electrodes. The ionic conductivities were obtained from bulk resistance that was measured by ac complex impedance analysis using a Solartron 1255 frequency response analyzer (FRA) over the frequency range of 100 Hz to 1 MHz.

3. Results and discussion

3.1. Characteristics of normal PVdF membrane prepared with no solvent pre-evaporation process and no stretching

Firstly, normal porous PVdF membrane as a reference was prepared with simple phase inversion method. The ionic conductivity of the normal porous PVdF membrane was 7.2×10^{-4} S cm⁻¹. The tensile strength of the porous membrane was measured to be 11.5 MPa, and it is much lower than that of conventional PE separator (~100 MPa). Fig. 1 presents the morphology of top side, cross-section, and bottom side of the normal porous membrane. The cross-section of the membrane shows sponge-like small micro-pores with a diameter in the range 0.1–1.0 μ m. The pores are generated during the solvent and non-solvent exchange process in the coagulation bath.

3.2. Physical properties of the membrane (prepared with solvent pre-evaporation process)

The normal porous PVdF membrane does not possess sufficient tensile strength for commercial utilization. Solvent

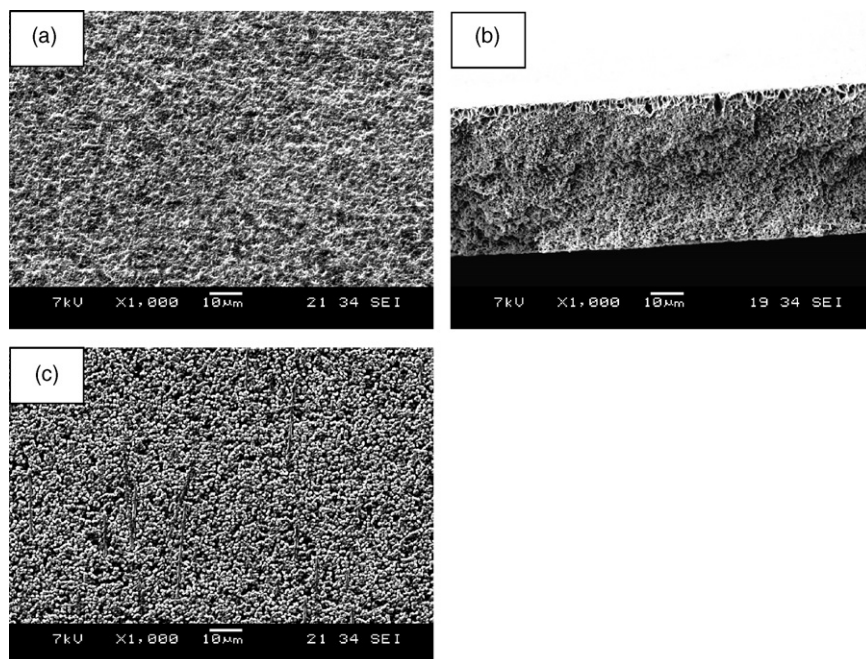


Fig. 1. SEM images of the normal porous PVdF membrane: (a) top side (b) cross-section (c) bottom side.

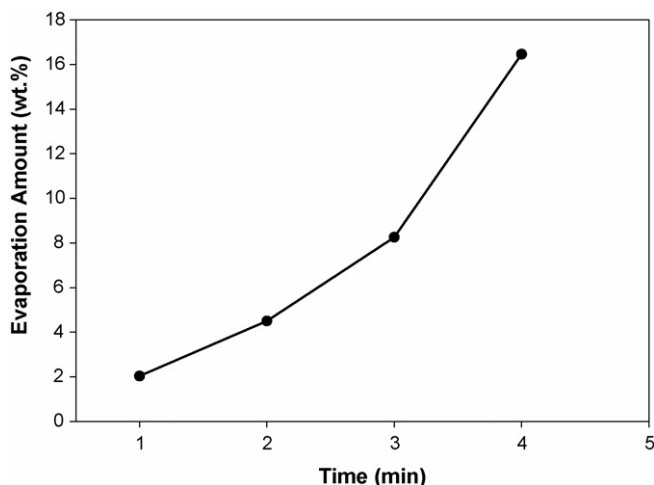


Fig. 2. Evaporation of the solvent of cast PVdF membrane with increase of pre-evaporation time.

pre-evaporation process was newly introduced to enhance tensile strength of the membrane prior to phase inversion process in a coagulation bath. By introduction of solvent pre-evaporation process, the structure of the membrane can be denser and the crystallinity of the membrane can increase. The evaporation amount of the solvent during the cast is plotted in Fig. 2. The evaporation was increased with increase in the solvent pre-evaporation time. After 4 min evaporation, 16.5 wt.% of DMF was lost from the cast polymer solution. Fig. 3 shows the cross-sectional morphologies of the porous membrane which have undergone the solvent pre-evaporation process. The pore diameter of the membrane is about 0.3–1.0 μm and macro-pores are also observed in the upper side of the

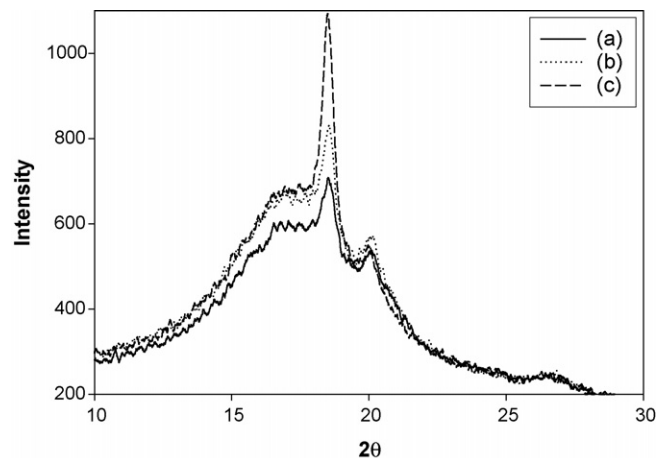


Fig. 4. X-ray diffraction intensity patterns of the membranes: (a) normal porous membrane; (b) membrane prepared with solvent pre-evaporation at 90 °C for 2 min; (c) membrane prepared with solvent pre-evaporation at 90 °C for 4 min.

membrane as shown in Fig. 3(c) and (d). This represents that the evaporated solvents were trapped at the upper side of the membrane with solvent pre-evaporation. It is clearly observed in Fig. 3 that the structural density of the membrane is increased with the solvent pre-evaporation. The solvent pre-evaporation condition may alter the crystal phase of PVdF which has important effect on the physical properties of the membrane. As shown in Fig. 4, the intensity of the diffraction peak of the membrane is increased with solvent pre-evaporation, which is indicative of the increase of crystallinity of the membrane.

The increase of crystallinity with solvent pre-evaporation can also be evidenced from the heat of fusion of the samples. Fig. 5

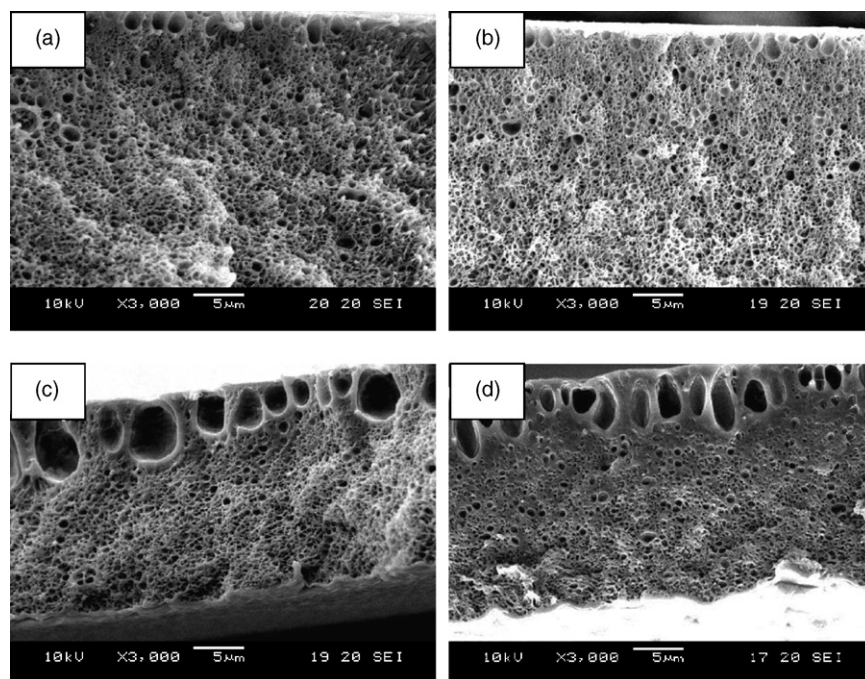


Fig. 3. Scanning electron micrograph of the porous PVdF membranes prepared with solvent pre-evaporation: (a) cross-sectional morphology of the membrane with 1 min solvent pre-evaporation; (b) cross-sectional morphology of 2 min solvent pre-evaporation; (c) cross-sectional morphology of the membrane with 3 min solvent pre-evaporation; (d) cross-sectional morphology of the membrane with 4 min solvent pre-evaporation.

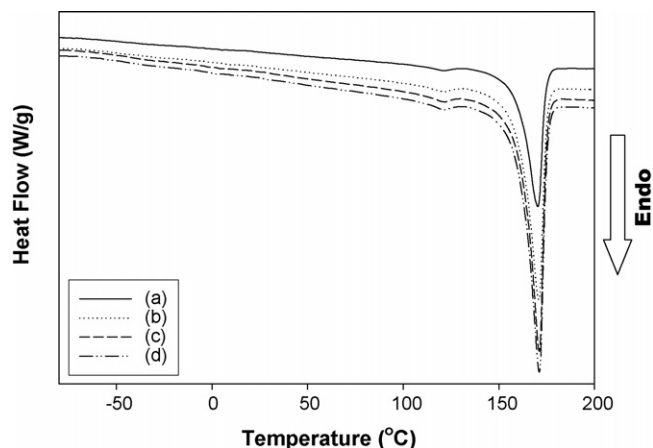


Fig. 5. DSC thermograms of the membranes; (a) solvent pre-evaporation at 90 °C for 1 min; (b) solvent pre-evaporation at 90 °C for 2 min; (c) solvent pre-evaporation at 90 °C for 3 min; (d) solvent pre-evaporation at 90 °C for 4 min.

shows that the heat of fusion of the crystalline phase in the membranes increases with solvent pre-evaporation.

3.3. Tensile strength and electrochemical properties of the membrane

The tensile strength of the membrane treated additionally with solvent pre-evaporation process was gradually enhanced with the solvent pre-evaporation as demonstrated in Fig. 8. This enhancement of tensile strength is mainly attributed to dense morphology of the prepared membrane. Its higher crystallinity could also contribute to an increase of tensile strength.

Fig. 9 shows the ionic conductivities for the membrane soaked in 1 M LiPF₆ in EC/DEC/PC (30/65/5, by vol.). The ionic conductivity of the membrane based on the additional

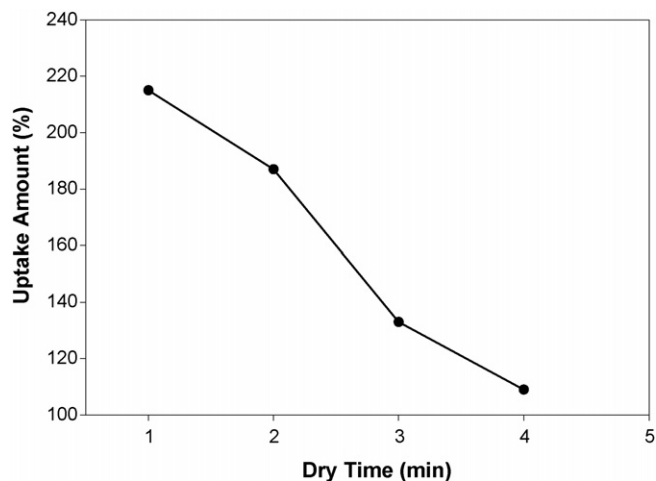


Fig. 6. Uptake amount of electrolyte solution of the membrane.

solvent pre-evaporation process (1 min evaporation) shows $3.4 \times 10^{-4} \text{ S cm}^{-1}$ and the ionic conductivity of the membrane prepared with 4 min solvent pre-evaporation process is $6.1 \times 10^{-5} \text{ S cm}^{-1}$. As shown in Fig. 9, the ionic conductivities of the membrane are decreased with increase of the solvent pre-evaporation time. The ionic conductivities of such polymer membranes are mainly influenced by the uptake of electrolyte solutions by the polymer membranes. The uptake amount of the electrolyte solution into the membrane is decreased with increase of the solvent pre-evaporation time due to its dense morphology. From Fig. 6, it is found that the uptake amount of the electrolyte solution was 215% of the matrix membrane for the membrane prepared with 1 min solvent pre-evaporation while the membrane prepared with 4 min solvent pre-evaporation showed uptake only 109% of the matrix membrane.

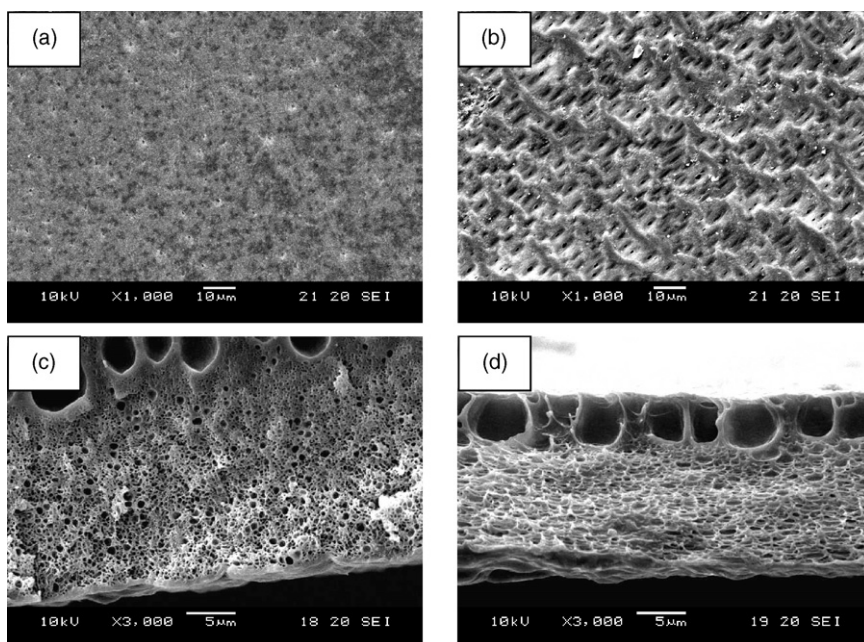


Fig. 7. Scanning electron micrograph of the membranes with uni-axial stretching: (a) top side of the membrane before stretching (b) top side of the membrane after stretching (c) cross-section of the membrane before stretching (d) cross-section of the membrane after stretching.

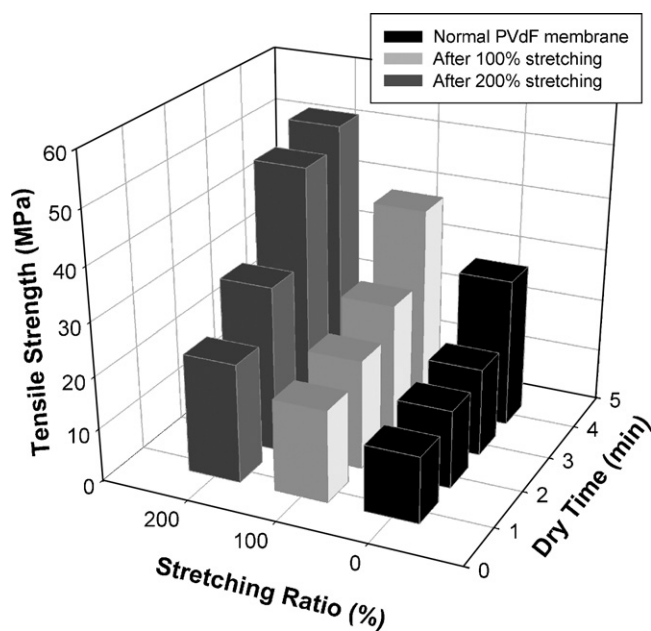


Fig. 8. Tensile strength of the membranes prepared with solvent pre-evaporation and stretching ratio.

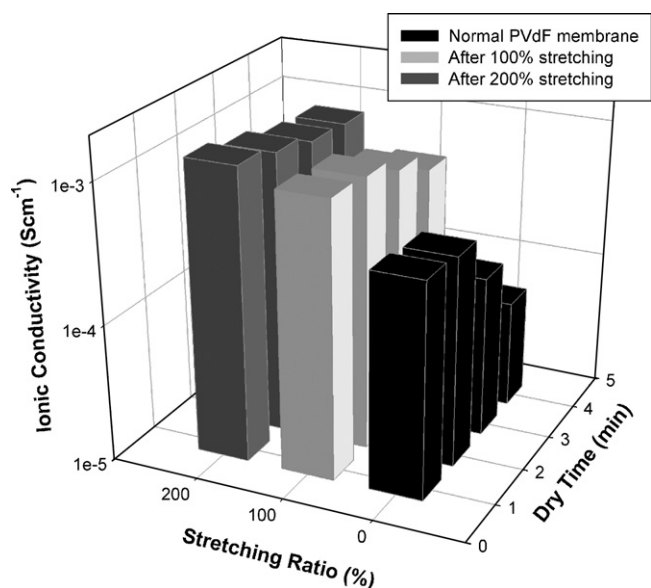


Fig. 9. Ionic conductivities of the membranes prepared with solvent pre-evaporation and stretching ratio.

3.4. Characterization of the membrane prepared with uni-axial stretching

It is expected that there are two kinds of positive effect on the tensile strength and ionic conductivities of the membrane from uni-axial stretching: Mechanical stretching can open and extend pores of the unstretched membrane. Hence, their uptake amount will increase. It can also enhance crystallinity of the membrane

due to their chain orientation and thereby the tensile strength may increase. Fig. 7 shows the cross-sectional SEM images of the membrane prepared with uni-axial stretching. The stretched membrane shows more extended structure of the pore as shown in Fig. 7(b) and (d) compared with the membranes prepared without stretching as shown in Fig. 7(a) and (c). The membranes prepared with stretching show enhanced tensile strength compared with the membranes prepared without stretching. The results of the tensile strength of the membranes are presented in Fig. 8, and the tensile strength is found to increase with the degree of stretching. The tensile strength of the porous PVdF membrane prepared with 1 min solvent pre-evaporation process was 12.6 MPa. After stretching, the tensile strength of the membrane is increased steadily with the extent of stretching. With increase of stretching ratio the uptake amount of the electrolyte solution was also increased. From Fig. 9, the ionic conductivity of the membrane prepared with 4 min solvent pre-evaporation could increase from 6.1×10^{-5} to 8.6×10^{-4} S cm⁻¹ with simple additional stretching.

4. Conclusions

In this study, we prepared and characterized the membrane prepared via phase inversion method including additional special solvent pre-evaporation and uni-axial stretching processes. The high ionic conductivity of the membrane could be achieved through a high uptake of electrolyte solution in the pores resulting from uni-axial stretching. The tensile strength of the membrane was also increased by introduction of the additional solvent pre-evaporation and uni-axial stretching processes. These processes could lead to a formation of dense structure and higher crystallinity of the membrane. It is suggested that this specially prepared membrane can be a good candidate for the separator of lithium rechargeable batteries.

Acknowledgement

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