

Short communication

Enhancement of the mechanical properties of PVdF membranes by non-solvent aided morphology control

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Abstract

A porous membrane based on poly(vinylidene fluoride) (PVdF) is prepared by the addition of a non-solvent before the phase-inversion step and it is stretched uni-axially to achieve high mechanical strength without sacrificing high ionic conductivity. The tensile strength of the PVdF membrane is 23 MPa without stretching, which is around twice that of a PVdF membrane made without addition of non-solvent before phase inversion. The former membrane can be stretched by up to 350% at room temperature and there by its tensile strength is increased to 126 MPa. In addition, the ionic conductivity is greatly enhanced due to an increase in porosity. The discharge capacity of the cell based on the stretched PVdF membrane is around 90% of the initial discharge capacity after 200 cycles.

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1. Introduction

The separator plays an important role in rechargeable lithium batteries since it keeps the positive and negative electrodes apart to prevent electrical short-circuits. It also transports ionic charge carriers during cell operation cell [1–3].

Poly(ethylene) (PE)-based separators have been generally used in conventional lithium secondary batteries. Whereas they have good mechanical properties and also good thermal properties, which effectively prevent thermal runaway resulting from electrical short-circuits, they have some disadvantages that include poor compatibility with liquid electrolytes and high manufacturing cost [4].

Unfortunately, however, there have been few investigations of alternative material-based separators that can enhance compatibility with liquid electrolytes without sacrificing mechanical and thermal properties. A PVdF-based separator has been considered as a possible candidate to replace PE-based separators because of its higher compatibility with liquid electrolytes and also its good processibility for phase inversion which is known to

be a versatile and simple technique for the preparation of porous polymeric membranes. The properties of membranes prepared by the phase-inversion process are mainly determined by their structure obtained during membrane formation [5–8]. Nevertheless, PVdF-based separators manufactured by phase inversion still suffer from low mechanical strength.

In our previous work [3], we demonstrated an enhancement in ionic conductivity and mechanical strength of a PVdF membrane by utilizing both conventional phase inversion and a mechanical stretching process with new solvent pre-evaporation process. In the present study, an attempt is made to enhance further the mechanical strength of PVdF-based separators by modification of the phase-inversion process developed earlier.

2. Experimental

2.1. Materials and preparation of membranes

A homopolymer of PVdF (SOLEF6020; average molecular weight: 320,000) was dissolved in *N,N*-dimethylformamide (DMF, Aldrich). A polymer solution was prepared by heating a mixture of PVdF and solvent (1:4 in weight ratio) at 70 °C for 5 h. Then, an appropriate amount of distilled water was added with

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stirring. The resulting solution was cast on a glass plate by means of a doctor blade with a gap of 20 μm . The cast solution was dried in an oven at 90 °C for 3 min for solvent pre-evaporation and then the film was immersed in a coagulation bath that was filled with a non-solvent (distilled water) for 6 h for phase inversion to generate pores.

Two different membranes were prepared by adding different amounts of non-solvent (distilled water), namely, 1 and 5 wt.% to the PVdF solution before conducting the phase-inversion process; the membranes are denoted as PVdF1 and PVdF5, respectively. All three components (PVdF, DMF, non-solvent) are only miscible over a small concentration range of less than 5 wt.% added water. When more water was introduced, PVdF was not miscible in DMF. The film was washed with methanol to remove residual traces of solvent and then dried at 30 °C under vacuum for 24 h.

2.2. Investigation of morphology

The morphologies of the top and bottom surfaces of the membranes were observed with a low-voltage, field emission scanning electron microscope (FESEM, FEI, Sirion, Netherlands). For taking the cross-sectional SEM images, samples were obtained by fracturing in liquid nitrogen.

2.3. Measurement of membrane porosity

The pore-size distribution of each membrane was measured with a mercury porosimeter (Autopore IV 9500, Micromeritics, USA). In order to minimize experimental error, three same samples of each membrane were tested and the average value was taken.

2.4. Tensile strength

The tensile strength of the membrane was determined by using an Instron 5583 Tensile Tester. The membrane was stretched uni-directionally as the clamps moved apart from each other at a constant rate of 10 mm per min. The stretch ratio was determined by dividing the final length of the stretched portion of film by its initial length before stretching.

2.5. X-ray diffraction analysis

X-ray diffraction (XRD) measurements were conducted to evaluate the crystallinity of the membrane. A JEOL 8030 X-ray diffractometer with a nickel filtered Cu $K\alpha$ radiation was used at room temperature (power: 30 kV/60 mA, scan range: $2\theta = 3\text{--}60^\circ$, scan speed: 3°min^{-1} , step size: 0.01°).

2.6. Electrical measurements

The PVdF membranes, immersed in an electrolyte of 1 M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC)/propylene carbonate (PC) [30/65/5, v/v/v] (Cheil Industries, Korea), were sandwiched between two stainless-steel (SS) electrodes. The ionic conductivity of each membrane was

obtained from the bulk resistance. The latter 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. Membrane morphology

In general, both the mechanical property and the ionic conductivity of a membrane are strongly dependent on its morphology. In order to achieve high mechanical strength without sacrificing ionic conductivity, it is required to control the morphology of the membrane. In a previous work [3], it was found that the limit to the mechanical strength of the membrane was due to the presence of large pores in the upper side (i.e., the opposite side to the substrate) of the cast membrane. Thus, a modified preparation method to suppress the formation of such pores is attempted in this study.

The porous membranes were prepared by the phase-inversion method. This process creates a polymer-rich phase that forms the solid membrane structure and a polymer-poor phase that forms the liquid-filled pores of the membrane [7]. Most of the solvent in the membrane pores is eventually replaced by the non-solvent. The resulting morphology of the membrane will be mainly dependent upon the relative amount of solvent and non-solvent, which subsequently influences the exchange rate during phase inversion.

Scanning electron micrographs of the cross-sectional morphology of the membranes prepared by the solvent pre-evaporation and the subsequent phase inversion are presented in Fig. 1. Many large pores are present at the upper side of the cross-section of the normal PVdF membrane that is produced without addition of the non-solvent to polymer solution before the phase-inversion step, see Fig. 1(a). The number of these large pores is much reduced for the PVdF1 and PVdF5 membranes produced with the addition of non-solvent before the phase-inversion step, as shown in Fig. 1(b) and (c). The addition of non-solvent hinders the mutual diffusion between solvent in the coagulation bath and the non-solvent in the cast film, and thus induces a delay in phase separation [7]. As a result, the PVdF1 and PVdF5 membranes exhibit a slow phase inversion and the number of large pores at the upper side is significantly reduced, whereas the membranes based on normal polymer solution undergo a rapid phase inversion to form large pores in this region.

3.2. Mechanical properties of uni-axially stretched membrane

By uni-axial stretching, it is possible to open and extend the pores of the membrane. This can lead to an increase in the uptake of electrolyte and also to an enhancement of crystallinity by chain orientation of the membrane accompanied by an increase in mechanical strength [3].

The stress–strain curves of the non-stretched and stretched PVdF1 and PVdF5 membranes are presented in Fig. 2. The

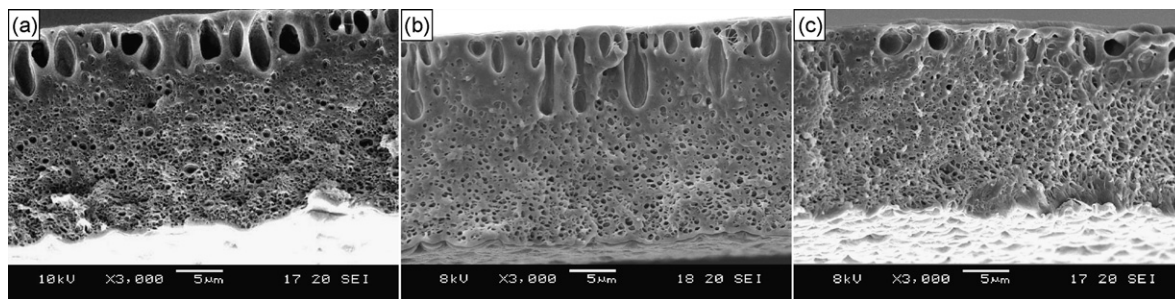


Fig. 1. Scanning electron micrographs of cross-sections of PVdF membranes: (a) normal PVdF; (b) PVdF1; (c) PVdF5.

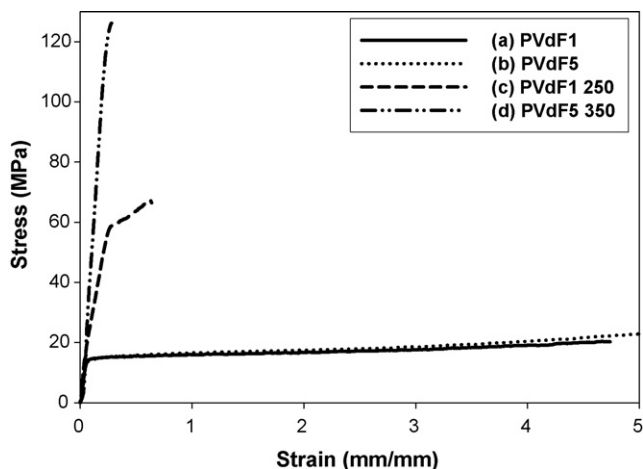


Fig. 2. Strain–stress curves of PVdF membranes: (a) PVdF1; (b) PVdF5; (c) PVdF1 after 250% stretching; (d) PVdF5 after 350% stretching.

two membranes can be stretched to 250 and 350% of the original, respectively. These extensions are greater than that for a PVdF membrane made without addition of non-solvent before the phase-inversion step because of the significant reduction in the number of large pores at the upper side of the cross-section of the membrane. The tensile strength and thickness of the membranes are listed in Table 1. The thickness and width of the uni-axially stretched membrane decreases with stretching ratio, while the length of the membrane is increased in the stretching direction. The PVdF5 sample, which does not have a significant number of large pores at the top side of the cross-section, and is stretched to 350%, shows a tensile strength of 126 MPa, which is much higher than that (56 MPa) of the membrane that has been made without addition of the non-solvent before phase inversion, as shown in the previous work [3]. This tensile strength is actually higher than that of the conventional PE separator used in lithium rechargeable batteries.

The XRD patterns of (a) normal PVdF membrane, (b) 100% stretched PVdF membrane (PVdF100), (c) 200% stretched

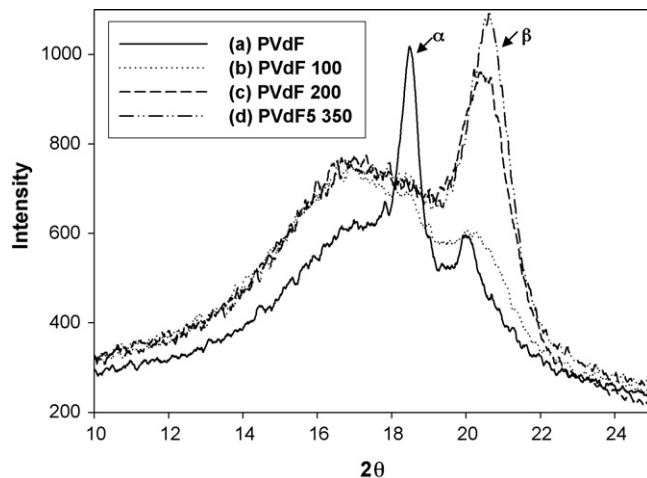


Fig. 3. X-ray diffraction patterns of membranes: (a) normal PVdF membrane; (b) PVdF 100; (c) PVdF 200; (d) PVdF5 350.

PVdF membrane (PVdF200), and (d) PVdF5 350 are presented in Fig. 3. The crystallinity of the membrane increases with stretching, which contributes to further enhancement of the mechanical strength. The conversion of α -crystals to β -crystals in the PVdF membrane with uni-axial stretching at room temperature is also shown in Fig. 3 and this conformational change assists in inducing further chain orientation [9].

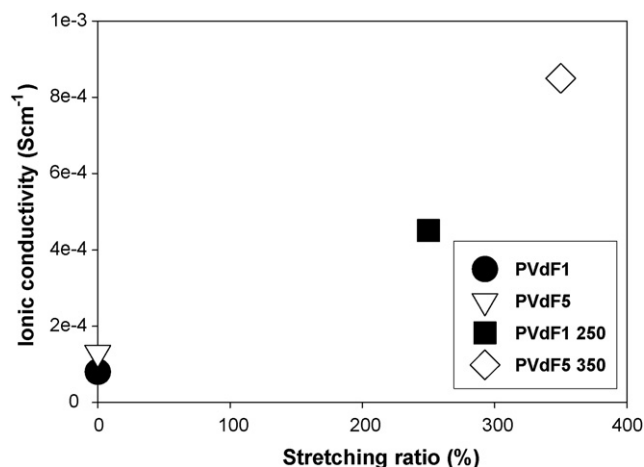


Fig. 4. Ionic conductivity of PVdF membrane with stretching ratio.

Table 1
Tensile strength and thickness of membrane

	PVdF1	PVdF1 250	PVdF5	PVdF5 350
Tensile strength (MPa)	20	65	23	126
Thickness (μm)	49	21	42	16

3.3. Electrochemical properties of membranes

The ionic conductivities increase with the stretching ratio of the membranes, as shown in Fig. 4. The morphology of the uniaxially stretched PVdF5 350 is displayed in Fig. 5. The highly stretched PVdF5 350 has an extended pore shape in the stretching direction, as shown in the top, cross-section and bottom regions, see Fig. 5(a)–(c), respectively. The change in porosity with increase in stretching is shown in Table 2. This feature will result in enhanced uptake of liquid electrolyte. The ionic conductivity of the 350% stretched PVdF membrane with higher porosity that was treated with non-solvent before the phase inver-

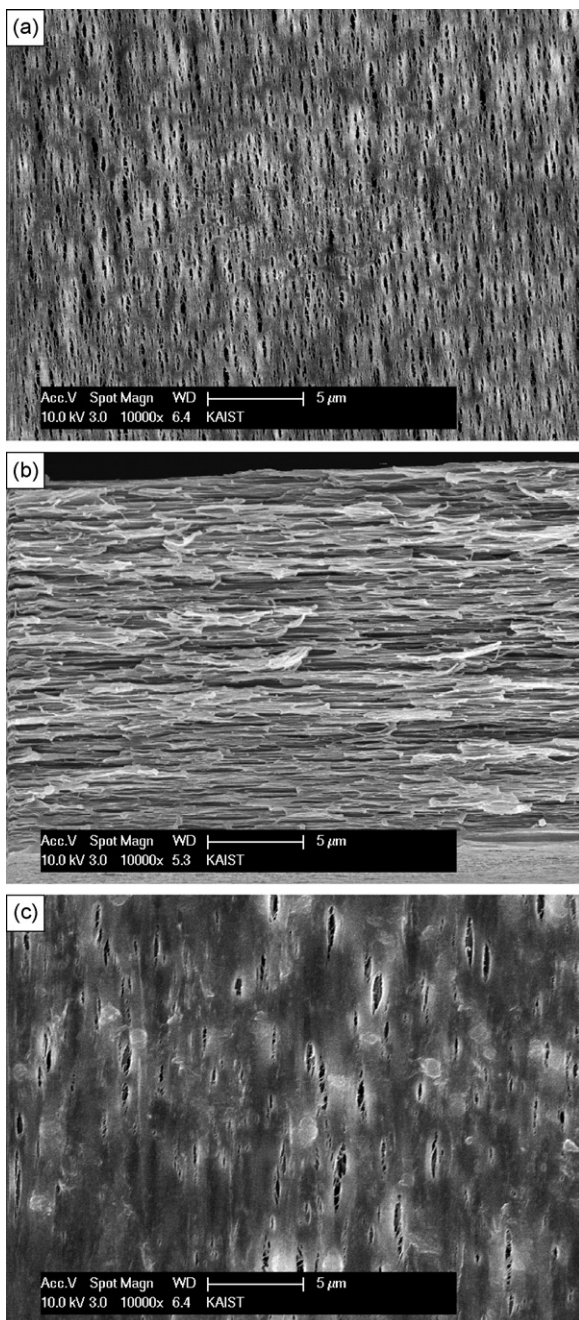


Fig. 5. Scanning electron micrographs of (a) top, (b) cross-section and (c) bottom side of PVdF membrane after uni-axial stretching.

Table 2
Porosity of PVdF membrane

	Porosity (%)
PVdF1	34
PVdF1 250	40
PVdF5	53
PVdF5 350	66

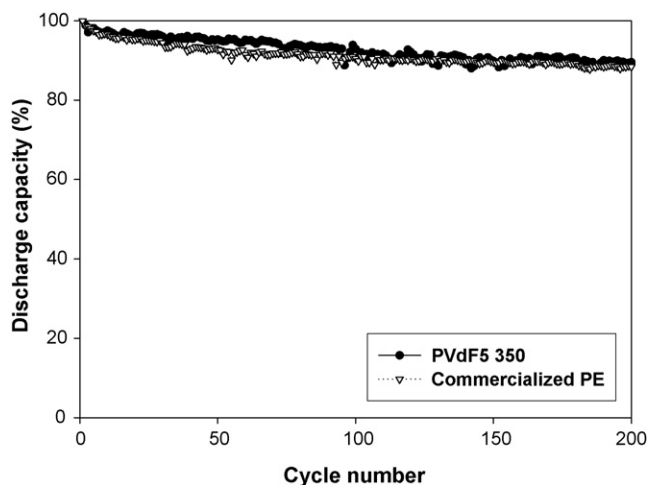


Fig. 6. Cyclic performance of cells based on PVdF5 350 and commercialized PE.

sion step is $8.5 \times 10^{-4} \text{ S cm}^{-1}$, which is almost similar to the previously reported value for the stretched membrane without such treatment.

In order to evaluate the electrochemical performance of a lithium-ion cell using the stretched PVdF membrane, a graphite/PVdF5 350 membrane (EC/DEC/PC/VC with 1M LiPF₆)/LiCoO₂ cell was fabricated. A cycling test of the unit cell was carried out at a constant current density 1.0 mA cm^{-2} (C/2 rate for charge–discharge) and with cut-off voltages of 3.0 and 4.2 V. The resulting charge–discharge curves are presented in Fig. 6. After 200 cycles, the discharge capacity of the cell based on the PVdF5 350 membrane is 90% of the initial value, while a unit cell based on the commercialized PE separator gives 88% after the same number of cycles. This suggests that the PVdF5 350 membrane is a promising candidate for practical application in lithium secondary batteries.

4. Conclusions

The morphology of the PVdF membrane is controlled with addition of a non-solvent to the polymer solution before the phase-inversion step to achieve high mechanical strength in the stretched membrane. Elimination of large pores at the upper side the membrane significantly contributes to enhancing the mechanical strength. The tensile strength of the stretched PVdF membrane is prepared with addition of non-solvent before phase-inversion, is higher than that of a conventional PE separator which is presently commonly used for lithium secondary batteries. Stretching of the morphology controlled membrane can also enhance the ion conductivity with the aid of the increase in the porosity.

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