

New Separators Based on Non-Polyolefin Polymers for Secondary Lithium Batteries

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Abstract : New porous separators based on non-polyolefin materials including the blend of poly (vinyl chloride) (PVC)/poly (vinylidene fluoride-co-hexafluoropropylene) (P(VdF-co-HFP)/poly(methyl methacrylate) (PMMA), and the porous separator based on poly (vinylidene fluoride) (PVdF) were prepared by phase inversion method. The porosity and morphology were controlled with phase inversion rate, which is governed by the relative content of non-solvent and solvent in coagulation bath. To enhance tensile strength, the solvent pre-evaporation and uni-axial stretching processes were applied. The ionic conductivity was increased with increasing stretching ratio, and tensile strength was increased with increasing solvent pre-evaporation time and stretching ratio. The 200% stretched PVdF separator showed 56 MPa of tensile strength, and the ionic conductivity of the stretched PVdF separator was $8.6 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C.

Key words : Separator, Membrane, Poly (vinyl chloride), Poly (vinylidene fluoride), Phase inversion, Stretching process, Lithium rechargeable battery.

1. Introduction

The separator plays an important role in lithium secondary batteries since it can keep the positive and negative electrodes apart to prevent electrical short circuits and also transport ionic charge carriers that are needed to complete the circuit during the passage of current in a cell. There are many requirements for the high performance of the separator: electronic insulation, minimal electric resistance, sufficient mechanical strength to allow easy handling, chemical resistance to degradation by electrolyte, and good wettability with electrolyte.^{1,2)}

The micro-porous polyethylene (PE) separator has been widely used in commercial lithium rechargeable batteries. However, the PE separator has some problems that it shows low affinity to liquid electrolytes and poor interfacial compatibility with electrode surface. Many studies have been progressed to enhance affinity of the separator to electrode. For this purpose, there have been reports that polyvinylidene fluoride (PVdF) can be used as coating material or matrix polymer for the separator.^{3,4)} In general, PVdF has a higher compatibility with liquid electrolytes than the PE separator and exhibits good solubility in many common organic solvents such as N,N-dimethylacetamide (DMA), N,N-dimethylformamide (DMF), N-methylpyrrolidone (NMP), and dimethylsulfoxide (DMSO). Therefore, PVdF can be used for the preparation of membranes by the non-solvent induced phase inversion process, which is a versatile and simple tech-

nique of preparation of polymeric membranes.^{5,6)} It is, however, to note that PVdF membrane that is prepared by phase inversion process usually shows low tensile strength. In connection with these, we have already reported the novel separator system based on PVdF and PE non-woven.⁷⁾

In this work, we prepared new micro-porous separators based on non-olefin polymers including PVC/P(VdF-co-HFP)/PMMA blend system and PVdF homopolymer by phase inversion method and they were uni-axially stretched. The electrochemical performance of the new cells was also evaluated.

2. Experimental

2.1 Preparation of the separator

The mixture of PVC (M.W. 233,000, Aldrich), P (VdF-co-HFP) (HFP 6%) and PMMA (M.W. 996,000, Aldrich) (8.5 : 1 : 0.5 in weight ratio) was firstly dissolved in dimethyl formamide (DMF, Aldrich). The polymer solution was cast on a glass plate and then immersed into the bath filled with water and DMF. The resulting membrane was vacuum dried at room temperature. The separator based on PVC was stretched uni-axially at a constant rate of 10 mm/min at 90°C.

For another type of membrane, a homopolymer of PVdF (M.W. 320,000 : SOLVAY) was dissolved in N, N-dimethylformamide (DMF, Aldrich) and the solution was 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 hrs. After complete dissolution, the solution was cast on a glass plate with doctor blade. The cast polymer films were dried in an oven at 90°C for 1 to 4 minutes and then immersed into a coagu-

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lation bath filled with non-solvent (distilled water) to generate micro-pores. Finally, the membranes were washed with methanol and dried at room temperature to remove the residual solvent. The membrane was stretched uni-axially at room temperature. The exact stretching ratio was determined by dividing the final length of the stretched portion of film to its initial length before stretching.⁸⁾

2.2 Physical properties of the separators

The morphology of the top and bottom surface of the membrane was observed using a low voltage field emission scanning electron microscope (FESEM, FEI, Sirion, Netherlands). For the SEM images of the cross section, the samples were prepared by fracturing the films in liquid nitrogen. Then, the samples were attached to a sample holder using conductive copper tapes and silver paste was applied in order to enhance electronic conductivity.

The pore size distribution of the specimens was measured with a mercury porosimeter (Autopore IV 9500, Micromeritics, USA).

The crystallinity of separator was investigated by X-ray diffraction analysis. The samples were subjected to X-ray diffraction analysis using JEOL 8030 X-ray diffractometer with a nickel filtered Cu K α radiation. All the WAXD experiments were performed at 2 theta between 3° and 60°. The crystalline diffractions and the amorphous component had been separated with a fitting program which allowed to estimate the crystallinity of the separators (Power: 30 kV/60 mA, scan range: 2 theta = 3–60°, scan speed: 3/min, step size: 0.01°).

The tensile strength of the separator 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.

2.3 Electrical measurements

The prepared separators were immersed in liquid electrolyte, 1M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC)/propylene carbonate (PC) [30/65/5, by vol.] (Samsung Cheil Industries, KOREA), and sandwiched between the two stainless-steel (SS) electrodes. All these experiments were carried out in a glove box under argon atmosphere with less than 0.5 ppm water. The ionic conductivities were obtained from bulk resistance that was measured by a.c. complex impedance analysis using a Solartron 1255 frequency response analyzer (FRA) over the frequency range of 100 Hz to 1 MHz.

The cycle test for the unit cell was performed by galvanostatic charge/discharge tester (TOSCAT-3000, Toyo System, Co.). Charge-discharge tests of the LiCoO₂/membrane/graphite cell (2032 type coin cell) were conducted in the voltage range 3.0–4.2 V at a constant current density of 1 mAcm⁻² (C/2 rate) with galvanostatically controlled equipment.

3. Results and Discussion

Porous PVC separator was firstly prepared with simple phase inversion method as a reference separator. Fig. 1 shows the cross-sectional morphologies of the PVC separators that are prepared with different concentration of PVC in

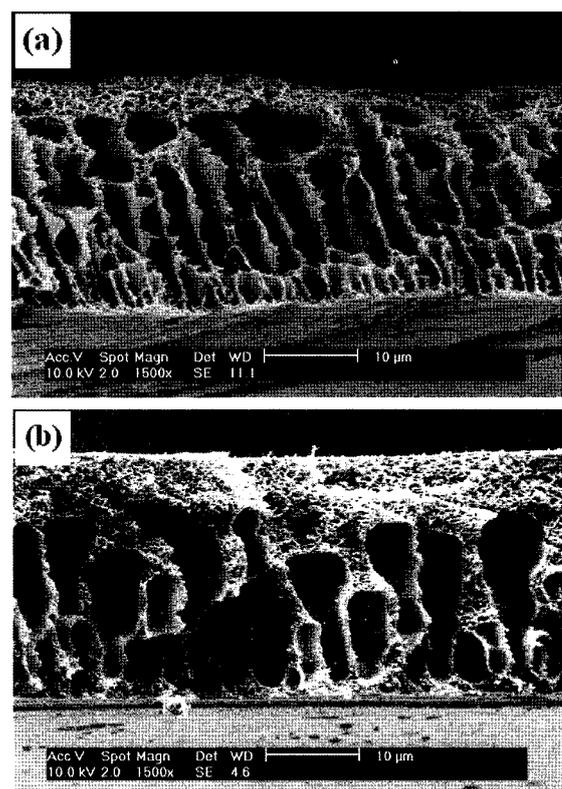


Fig. 1. Cross sectional morphologies of PVC separators with PVC concentration in polymer solutions (a) PVC11, (b) PVC13.

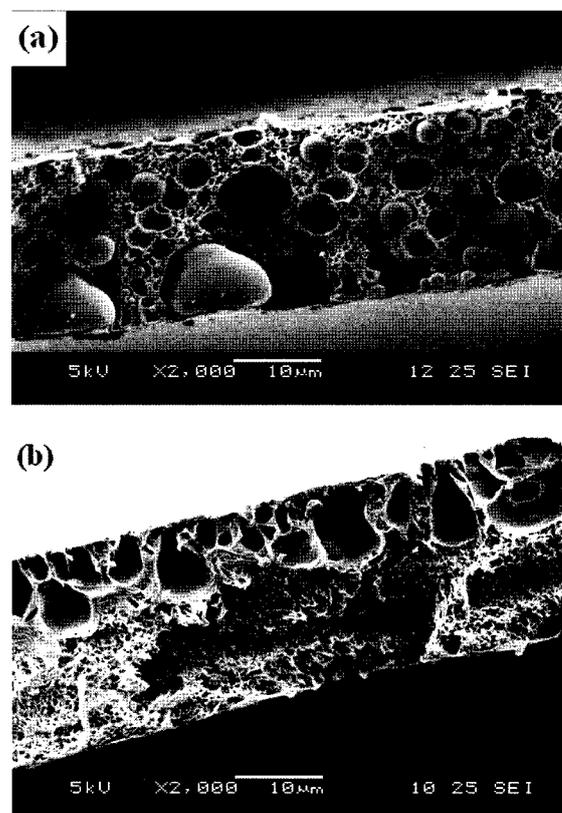


Fig. 2. Cross sectional morphologies of separators based on (a) PVC/P(VdF-co-HFP), and (b) PVC/P(VdF-co-HFP)/PMMA.

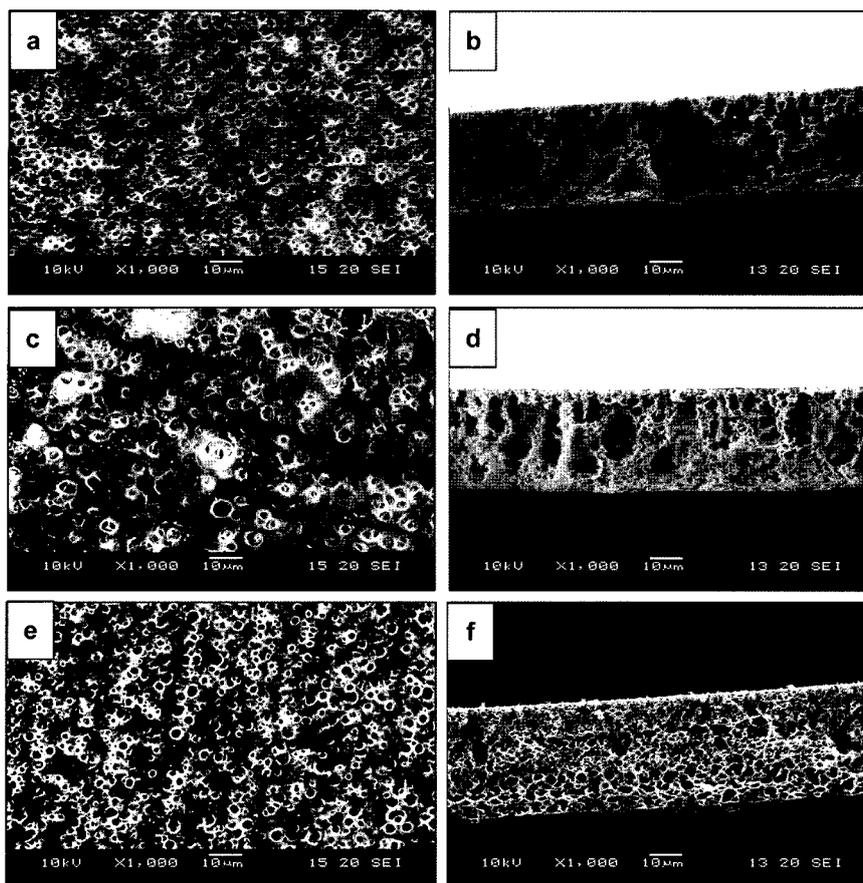


Fig. 3. Surface and cross sectional morphologies of the membranes prepared with different relative content of Water/DMF in coagulation bath: (a), (b): 10/0, (c), (d): 5/5, (e), (f): 2/8.

polymer solution. The pores are generated during exchange of the solvent in polymer solution and non-solvent in coagulation bath. The PVC separator prepared with 11 wt% of polymer solution (PVC11) shows more finger-like large pores in the cross sectional image of the separator than the separator based on 13 wt% polymer solution (PVC13). The ionic conductivity of PVC11 and PVC13 were measured to be $3.4 \times 10^{-4} \text{ S cm}^{-1}$ and $0.7 \times 10^{-4} \text{ S cm}^{-1}$ respectively. The difference in the ionic conductivity between PVC11 and PVC13 is caused by the difference of the morphology and also the porosities of the separator.

The ionic conductivity of the PVC separator is found to be lower than that of the commercialized PE separator ($1 \times 10^{-3} \text{ S cm}^{-1}$). To enhance ionic conductivity, P(VdF-co-HFP) with good affinity to liquid electrolyte was introduced to PVC separator. Fig. 2 (a) shows the cross-sectional morphology of the separator prepared with PVC/ P(VdF-co-HFP) blend solution. As shown in Fig. 2 (a), P(VdF-co-HFP) is micro-phase separated in PVC matrix. To increase miscibility of PVC and P(VdF-co-HFP), PMMA that is expected to function as a compatibilizer, was additionally introduced. A typical SEM images of porous separator (PVC-based separator) based on the blend of PVC, P(VdF-co-HFP), and PMMA is presented in Fig. 2 (b) and it shows that they form a single phase with less population of the finger-like large pores.

In order to reduce the number of finger-like large pores that cause degradation in mechanical property, we tried to control the morphology of the membrane. The properties of the membrane made with phase inversion process are mainly determined by their structure produced during their formation process. In general, finger-like macro-void formation occurs under rapid polymer precipitation conditions and the void formation can be suppressed by increasing the viscosity of the casting solution.⁹ In this work, the mixture of non-solvent and solvent in a coagulation bath to slow down precipitation rate was used to generate sponge-like micro-pores.

Fig. 3 shows the morphologies of the PVC-based separators prepared with different non-solvent /solvent ratio in the mixture of solvent and non-solvent. Fig. 3 (a) and (b) show surface and cross sectional SEM images of PVC-based separator based on only non-solvent, water. Fig. 3 (c) and (d) represent morphologies of PVC-based separator prepared with the mixture of non-solvent (water) and solvent (DMF) (5/5). Fig 3 (e) and (f) are for PVC-based separator prepared with the mixture of non-solvent (water) / solvent (DMF) (2/8). With increase of the relative content of the solvent (DMF) in the mixture, the population of the finger-like large pores formed is decreased and it disappears eventually for the separator prepared with non-solvent (water) /solvent (DMF) (2/8). The increase of DMF content in the mixture hinders mutual

Table 1. The porosity and ionic conductivity of PVC separator with different relative content of Water/DMF in coagulation bath

Water/DMF	10/0	5/5	2/8
Porosity (%)	70	57	46
Ionic conductivity (Scm ⁻¹)	4.3 × 10 ⁻⁴	3.2 × 10 ⁻⁴	1.7 × 10 ⁻⁴

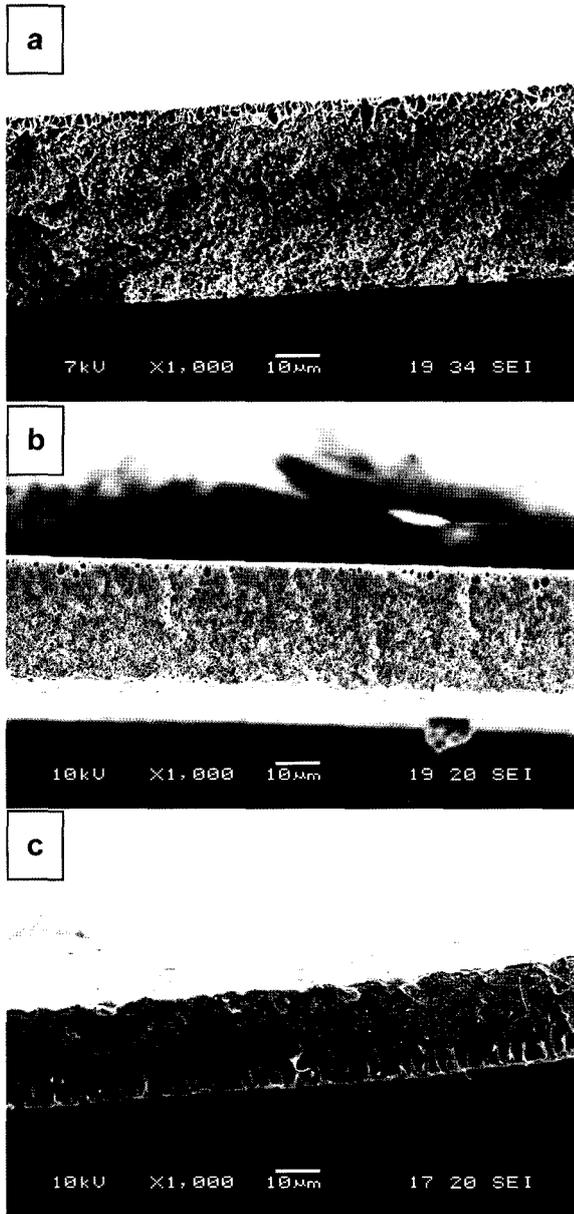


Fig. 4. Cross sectional morphologies of PVdF separators with solvent pre-evaporation time: (a) normal PVdF separator, (b) 2 min drying, (c) 4 min drying.

diffusion of solvent in the cast film and it makes the structure of the membrane more porous.

Table 1 shows the porosity and ionic conductivity of the PVC-based separator. The increase of DMF content in the mixture makes the number of finger-like pores and also the porosity of the PVC-based separator reduced. As a result, the ionic conductivity is lowered for the PVC-based separator with lower porosity than the PVC-based separator prepared

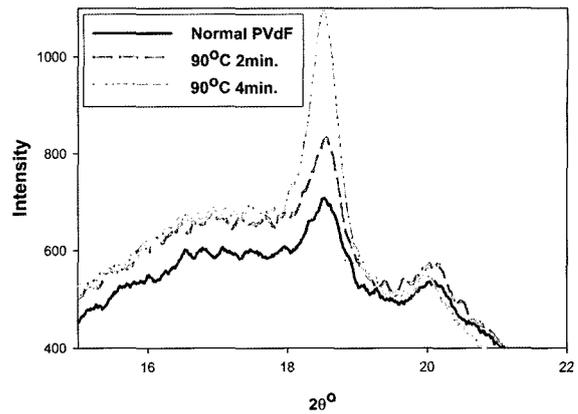


Fig. 5. Wide angle X-ray diffraction pattern of PVdF separators: (a) normal PVdF separator, (b) 2 min drying, (c) 4min drying.

with non-solvent water only.

In order to enhance ionic conductivity and mechanical strength, the membranes were uni-axially stretched. Mechanical stretching can open and extend pores of the non-stretched separator and thus their uptake amount will increase. It can also enhance crystallinity of the membrane by their induced chain orientation and thereby the mechanical strength will increase.¹⁾

In our previous work, we have demonstrated an enhancement of ionic conductivity and mechanical strength of the PVC separator by uni-axial stretching process.¹⁰⁾ The PVC-based separator shows a remarkable improvement in mechanical properties from 8 MPa to 52 MPa after high-temperature stretching, and the ionic conductivity was also increased with increased porosity of the separator.

The PVC-based separator showed good electrochemical and mechanical properties, however, it did not show good affinity to liquid electrolyte. In general, PVdF has a higher compatibility with liquid electrolytes than the PE separator but the PVdF separator that is made by phase inversion process shows low tensile strength. In our previous work, the solvent pre-evaporation process was taken to enhance crystallinity of the PVdF membrane in order to improve mechanical property.¹⁾ The mechanical property of normal PVdF separator prepared by phase inversion process is 12.7 MPa and after undergoing 4 min. solvent pre-evaporation processing the mechanical strength is increased to 28.2 MPa. The solvent pre-evaporation process could increase mechanical strength owing to the increase crystallinity of the separator. As shown in Fig. 4, by the introduction of solvent pre-evaporation process, the structure of the membranes becomes denser and thinner, and the crystallinity of the membrane becomes increased. The crystallinity of the PVdF separator prepared by solvent pre-evaporation is presented in Fig. 5. With increase of solvent pre-evaporation time, the crystallinity is found to increase. Fig. 6 shows that the enhancement of mechanical strength with increase of crystallinity and dense morphology of PVdF separator make ionic conductivity reduced. To enhance ionic conductivity and mechanical property of PVdF separator, the uni-axial stretching was also applied and the separator was stretched to 200% at room

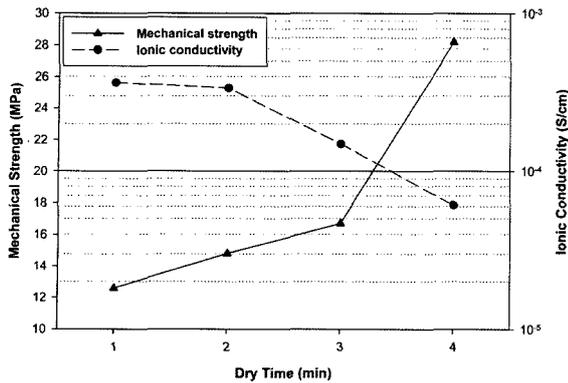


Fig. 6. Mechanical strength and ionic conductivity with drying time.

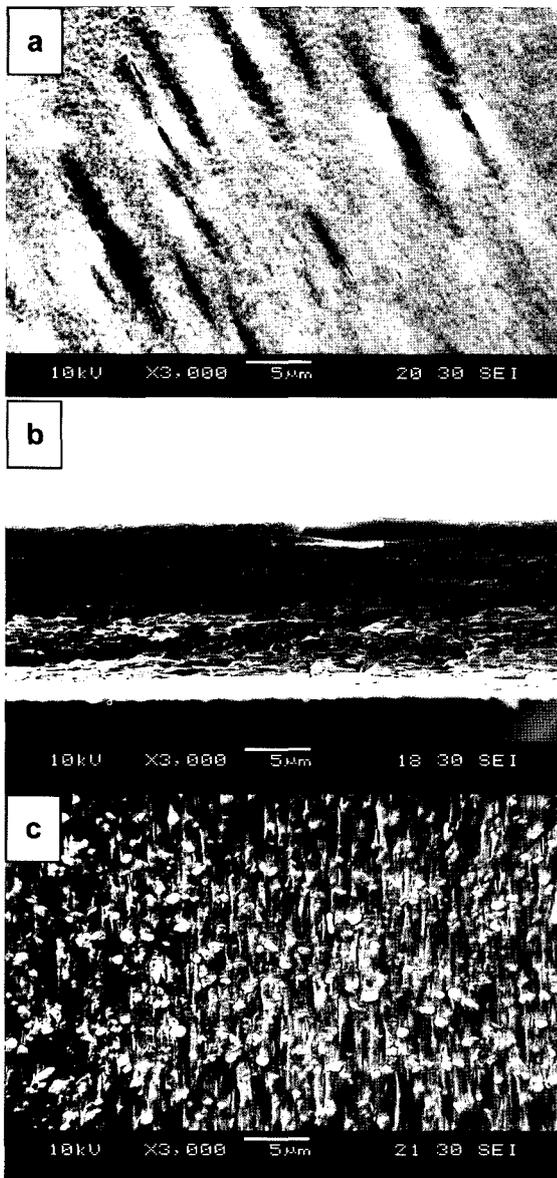


Fig. 7. SEM images of stretched PVdF separator: (a) top, (b) cross section, (c) bottom.

temperature. After uni-axial stretching, the mechanical property was increased to 56 MPa with chain orientation of PVdF

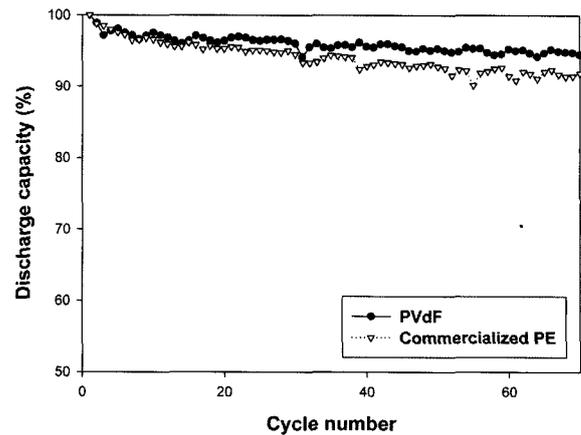


Fig. 8. Discharge capacity curves of the unit cells based on graphite/PVdF separator/LiCoO₂ and also graphite/PE separator/LiCoO₂ at C/2 rate.

and the ionic conductivity was also increased to 8.6×10^{-4} S cm⁻¹. The SEM morphology of the stretched separator is shown in Fig. 7 and it is found that the pores are stretched along the machine direction.

In order to evaluate the electrochemical performance of a lithium ion cell using the stretched PVdF separator, we fabricated a graphite/PVdF separator (EC/DEC/PC with 1 M LiPF₆)/LiCoO₂ cell. The cycling test of the unit cell was carried out at a constant current density of 1.0 mAcm⁻² (C/2 rate for charge-discharge) and with cut-off voltages of 3.0 and 4.2 V up to 70 cycles and the result is shown in Fig. 8. It is seen from this figure that the discharge capacity of PVdF separator after 70 cycles reaches 96% of the initial value. Considering that the unit cell based on the commercialized PE shows 93% of the initial discharge capacity after 70 cycles, it is suggested that the PVdF separator can be a promising candidate for the separator of secondary lithium batteries.

4. Conclusions

New porous separators based on PVC/P(VdF-co-HFP)/PMMA (PVC-based separator) and PVdF were prepared by phase inversion method and they were uni-axially stretched. The tensile strength and ionic conductivity are increased with stretching. The PVC-based separator shows good ionic conductivity and mechanical property from uni-axial stretching. PVdF separator with good affinity to liquid electrolyte exhibited high cyclic performance, suggesting that it can be a good candidate for the separator of lithium rechargeable batteries.

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