

Enhancement of the Ionic Conductivity and Mechanical Strength of Micro-porous Separator by Uni-axial Drawing

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(Received February 13, 2006 : Accepted February 24, 2006)

Abstract: A new porous separator based on poly(vinyl chloride) (PVC)/poly(vinylidene fluoride-co-hexafluoropropylene) (P(VdF-co-HFP))/poly(methyl methacrylate) (PMMA) was prepared by a phase inversion method. To enhance mechanical property, the membrane was stretched uniaxially at high temperature. Tensile strength and ionic conductivity were measured for various draw ratios. The tensile strength and ionic conductivity were increased with increasing draw ratio. The tensile strength of the separator reached 52MPa after stretching to draw ratio of 5, and the ionic conductivity of the separator was increased from 1.9×10^{-4} S/cm to 4.6×10^{-4} S/cm at 25°C. The stretched separator immersed in liquid electrolyte was electrochemically stable up to 4.7 V. The cell based on the stretched separator was maintained at about 99% of the initial discharge capacity after 10th cycle operation at 0.2C rate.

Keywords: Separator, Poly(vinyl chloride), Poly(vinylidene fluoride-co-hexafluoropropylene), Poly(methyl methacrylate), Phase inversion, Drawing process, Rechargeable lithium battery.

1. Introduction

A separator is a porous membrane placed between electrodes of opposite polarity, permeable to ionic flow but preventing electric contact of the electrodes.¹⁾ The main function of the separator is to keep the positive and negative electrodes apart to prevent electrical short circuits and at the same time allow rapid transport of ionic charge carriers that are needed to complete the circuit during the passage of current in an electrochemical cell.¹⁾ The micro-porous polyethylene(PE) separator has been widely used in commercial lithium rechargeable batteries. It has excellent porous structure, high mechanical strength, suitable shutdown temperature and high electrochemical stability.¹⁾ However The PE separator has problems that it has low affinity with liquid electrolytes and poor interfacial property with electrode surface.²⁾ In line with this, many studies have been progressed to provide a good electrolyte impregnating properties. There were reports that polyvinylidene fluoride(PVdF) was used as coating material or matrix polymer for this purpose.^{3,4)} Our group has also reported the novel separator system based on PVdF and PE non-woven.²⁾ To obtain a hydrophilic surface of membrane, grafting of hydrophilic organic monomer by surface modification such as plasma-treating has been performed.^{5,6)} Some groups have developed the composite membrane containing of various inorganic materials.⁷⁾

In this work, we fabricated the novel micro-porous membrane based on PVC/P(VdF-co-HFP)/PMMA ternary system

by phase inversion method. PVC was introduced to provide mechanical strength of polymer membrane. P(VdF-co-HFP) and PMMA were used for improvement of elongation property and affinity with liquid electrolyte of membrane. In addition, we employed high temperature drawing process to further to enhance mechanical strength and also to increase the ion pathway connectivity. The electrochemical performance of the cell based on the above membrane was also evaluated.

2. Experimental

2.1. Preparation of the separator

The solution of PVC(m.w. 233,000, Aldrich) and P(VdF-co-HFP) (HFP 6%) dissolved in dimethyl formamide (DMF) and PMMA(m.w. 996,000, Aldrich) dissolved in tetrahydrofuran(THF) were mixed. They were cast onto the glass plate and then immersed into the bath filled with water and DMF. The membrane was vacuum dried at room temperature. The separator was stretched uni-axially when the clamps move apart from each other at a constant rate of 10 mm/min at 90°C. 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. The Instron tensile tester equipped with the heat control chamber was used for stretching the membrane.

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2.2. Structural and mechanical property of the separator

The morphology of membrane was investigated by Scanning Electron Microscopy using the Philips SEM 535M. The specimens for the SEM images of the cross section of films were prepared by fracturing the corresponding unit cell. The pore size distribution of the specimens was measured with a mercury porosimeter (Autopore IV 9500, Micromeritics, USA). The pore size of a separator can usually be obtained according to the following equation.

$$D = -\left(\frac{1}{P}\right)4\gamma\cos\Psi$$

where D is the average diameter of the pores, P is the applied pressure, γ is the surface tension of mercury, and Ψ is the contact angle of mercury. The mechanical properties of the membrane were determined by using an Instron 5583 Tensile Tester. The testing was generally carried out along the MD at a cross head speed of 5 mm/min. The test samples were aged more than two weeks at room temperature. XRD measurements were done to evaluate crystallinity of the membrane. X-ray diffraction patterns were obtained with a Rigaku X-ray diffractometer using Ni-filtered Cu-K α ray at room temperature. (power=30 kV 60 mA, scan range: 2 theta=3~60°, scan speed: 3/min, step size : 0.01)

2.3. Assembly of the unit cell

The prepared separator was immersed in liquid electrolyte, 1 M LiPF $_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC)/propylene carbonate (PC) [30/65/5, by vol.] (Samsung Cheil Industries, KOREA). The immersed separator was lightly patted with a tissue to remove the liquid electrolyte on the film surface. The manufactured electrodes were immersed into the liquid electrolytes for 24 h before the cell assembly to fill the pores in the electrodes with the liquid electrolytes. Graphite carbon/immersed separator/LiCoO $_2$ cells were fabricated by sandwiching the separator between the graphite carbon anode and the LiCoO $_2$ cathode. The cells were finally packaged in an aluminized polyethylene bag and vacuum sealed in order to permit testing outside of a glove box. All these experiments were carried out in a glove box under argon atmosphere with less than 0.5 ppm water.

2.4. Electrical measurements

The Prepared separators were sandwiched between the two

stainless steel (SS) electrodes to measure the ionic conductivities. The ionic conductivities were obtained from bulk resistance measured by a.c. complex impedance analysis using a Solartron 1255 frequency response analyzer (FRA) over frequency range of 100 Hz~1 MHz. The pathway connectivity of the transported ions can be determined from n parameter measured from the dielectric loss spectra. The dielectric loss ($\log \epsilon''$) decreases as a function of \log frequency and the slope is $-n$. Generally, the case of $n < 1$ is reflective of the systems having random charge conducting paths across the sample dimensions that may or may not intersect each other. A value of $n = 0.5$ would suggest strong diffusion control and tortuous pathways. At the other extreme $n = 1$ corresponds to the sample dimensions in direct fashion and drift is dominant.^{8,9)}

The electrochemical stability of the electrolytes was determined by running a sweep voltammetry (applied voltage: 0~7 V, scan rate: 2 mV/s) on a two electrode where a stainless steel (SS304) was the working electrode, and a lithium electrode was the reference electrode. The impedance of the unit cell was measured using a Solartron 1255 FRA to obtain the information at the interface between the polymer electrolytes or separators and the electrodes. The change of the impedance with cycle number was also monitored. Charge/discharge tests for the unit cell were performed out by galvanostatic charge/discharge cycling tester (TOSCAT-3000, Toyo System Co.) at room temperature. The unit cell was typically cycled between 2.8 V and 4.2 V.

3. Results and Discussion

A typical scanning electron micrograph of a porous separator prepared with PVC, P(VdF-co-HFP), and PMMA by the phase inversion method is presented in Fig. 1. Most of the top side of the separator is found to have pores of various sizes compared with bottom side in Fig. 1(a). The bottom side does not possess pores since the casting was done on the glass plate. In order to enhance mechanical strength, we performed uniaxial drawing of PVC/P(VdF-co-HFP)/PMMA separator. Fig. 2 shows morphological changes of PVC/P(VdF-co-HFP)/PMMA separator after machine direction (MD) stretching at draw ratio of 5. With stretching, the pores of top side and cross section are changed into elliptical shape. After stretching, the pore size was also increased with draw ratio at the bottom side.

The ionic conductivity is calculated from the bulk resistance

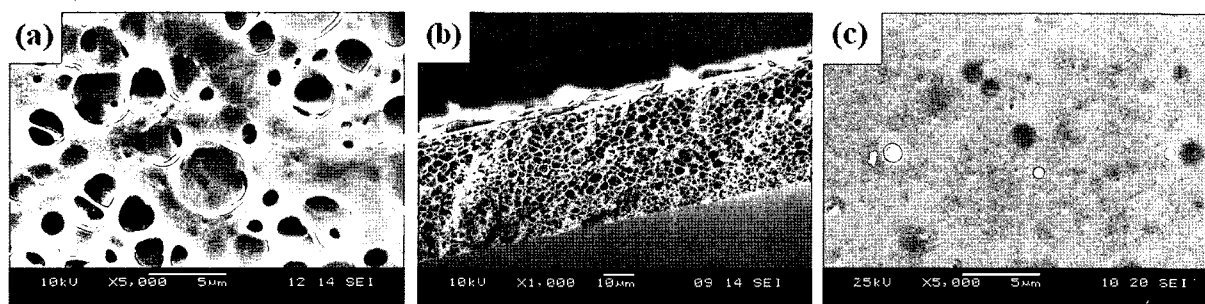


Fig. 1. Cross section and surface morphology of the bare PVC/P(VdF-co-HFP)/PMMA separator (a) top side (b) cross section (c) bottom side

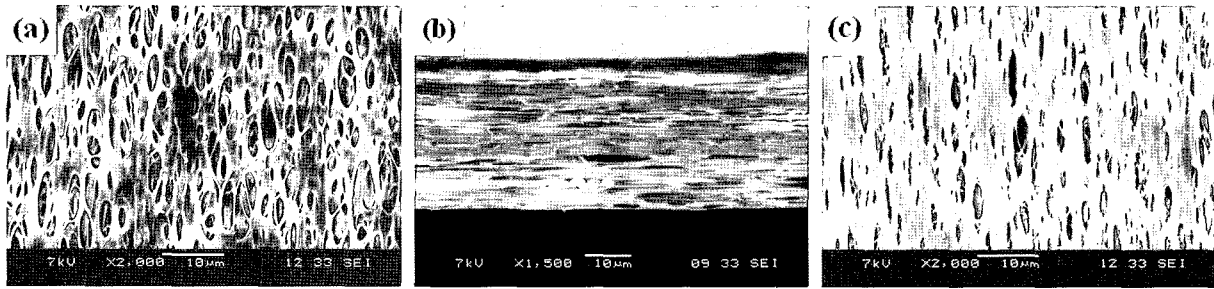


Fig. 2. Morphology of PVC/P(VdF-co-HFP)/PMMA separator stretched at draw ratio of 5 (a) top side (b) cross section (c) bottom side.

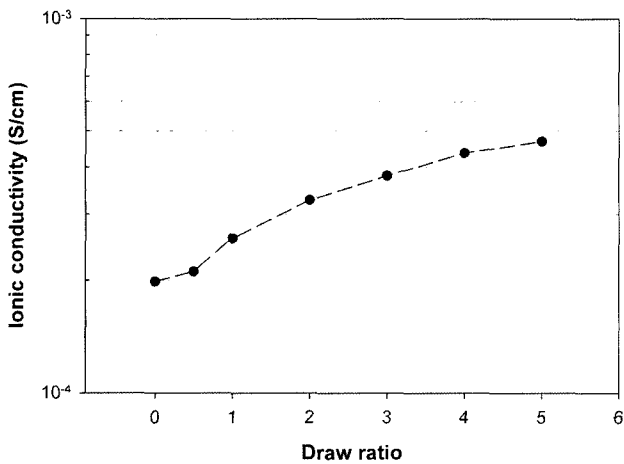


Fig. 3. Ionic conductivities of polymer electrolytes based on stretched PVC/P(VdF-co-HFP)/PMMA separators at room temperature.

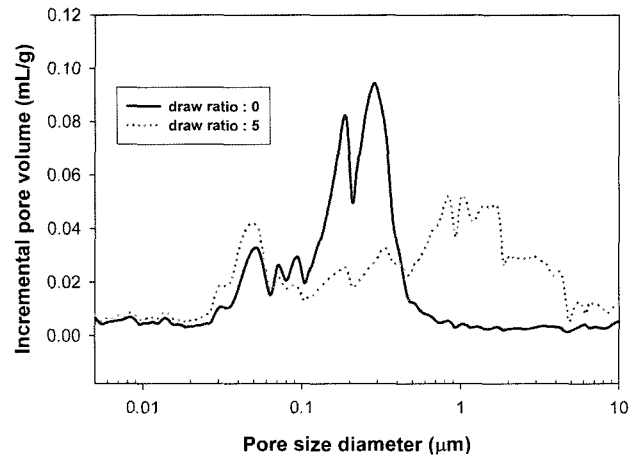


Fig. 4. The pore size distribution of PVC/P(VdF-co-HFP)/PMMA separators.

for separator of the same thickness. The influence of the membrane stretching on the ionic conductivity is shown in Fig. 3. At room temperature, the non-stretched membrane has the ionic conductivity of 1.9×10^{-4} S/cm and the ionic conductivity of 500% stretched membrane is 4.7×10^{-4} S/cm. It is considered that there are two main factors to influence on the ionic conductivity in this case. One is the porosity of separator to determine the amount of immersed liquid electrolyte and the other is pathway connectivity which represents the distance of ion movement between two electrodes.

From Fig. 4, in the case of non-stretched membrane, the most probable pore diameter is $0.2 \sim 0.3 \mu\text{m}$. After 500% stretching, the pore diameter is increased to around $1 \mu\text{m}$. The change of pathway connectivity of ion migration with draw ratio can be evaluated with the so-called n-parameter of polymer electrolyte.⁸⁾ From Fig. 5, n-parameter of the conventional PE separator is calculated to be 0.95, the n-value of non-stretched separator is 0.92, and the 500% stretched separator has n-parameter of 0.94. It is expected that the separator prepared by phase inversion method has the same good pathway connectivity as the conventional PE separator.

Fig. 6 shows stress-strain curve of the porous separator as a function of draw ratio. When a tensile speed of 5 mm/min was put on the separator in 25°C, stress at a break of the non-stretched separator was 8.6 MPa. With increase of draw ratio, tensile strength at a break and initial modulus were increased,

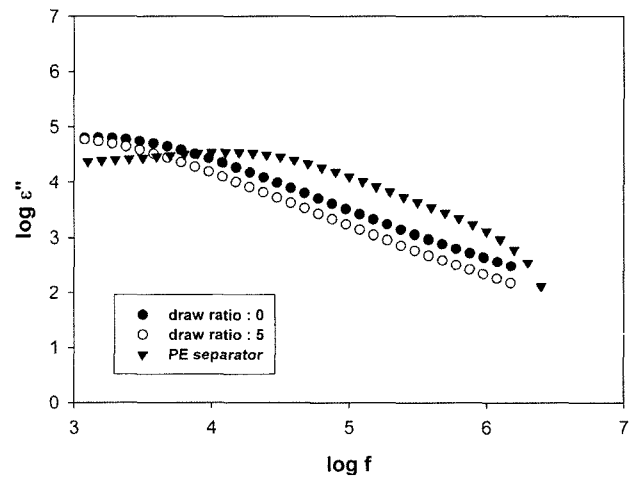


Fig. 5. The dielectric loss spectra of the conventional PE separator and PVC/P(VdF-co-HFP)/PMMA separators soaked with liquid electrolytes

but the maximum elongation was decreased. The increase of mechanical strength by the drawing process is attributed to increase of orientation of polymer chain.⁹⁾ Fig. 7 shows wide angle X-ray diffraction pattern of the separators with draw ratio of 0 and 5. The diffraction peaks at about 18° and 25° correspond to the various planes of orthorhombic unit cell of the matrix polymer.^{11,12)} The increase of intensity of the peak is indicative of the increase of chain orientation. It is obvious

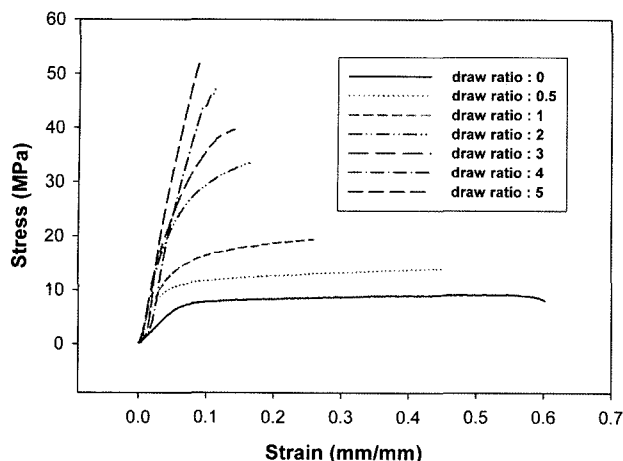


Fig. 6. The stress-strain curve of PVC/P(VdF-co-HFP)/PMMA separators with various draw ratios.

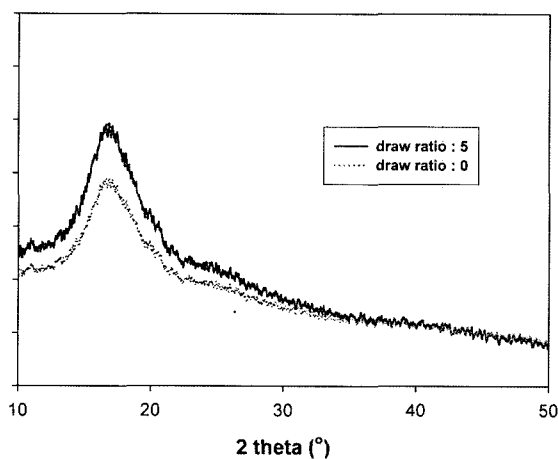


Fig. 7. Wide angle X-ray diffraction pattern of PVC/P(VdF-co-HFP)/PMMA separators.

that the peak intensity is increased with draw ratio.

Fig. 8 shows the result of linear sweep voltammetry (LSV) of the 500% stretched separator stretched immersed with liquid electrolytes. The separators were electrochemically stable up to 4.7 V, and then it can be suitably used for lithium rechargeable batteries.

In order to evaluate the electrochemical performance of a lithium ion cell using the separator, we fabricated a graphite/polymer electrolyte/LiCoO₂ cell. The charge/discharge curves for the pre-cycling are shown in Fig. 9. It was charged at a constant current density of 0.25 mA/cm² (C/10rate) to 4.2 V and discharged at 0.25 mA/cm² to 3.0 V. The cell showed an irreversible capacity of 15%. Fig. 10 shows the a.c. impedance spectra of the cell in a fully discharged state and in the spectra there is only one semicircle.

However, after pre-cycling the spectra exhibit another semicircle. This semicircle results from passivation films on both electrode surfaces.

Fig. 11 shows the charge/discharge curves with cycling for the given cell at 0.2C rate. At a low current rate (0.2C), the cell showed a good cyclic performance that the discharge capacity

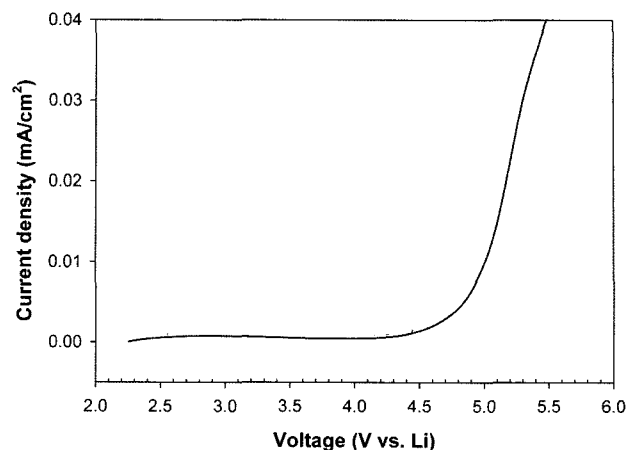


Fig. 8. Linear sweep of the cell based on polymer electrolyte based PVC/P(VdF-co-HFP)/PMMA separator.

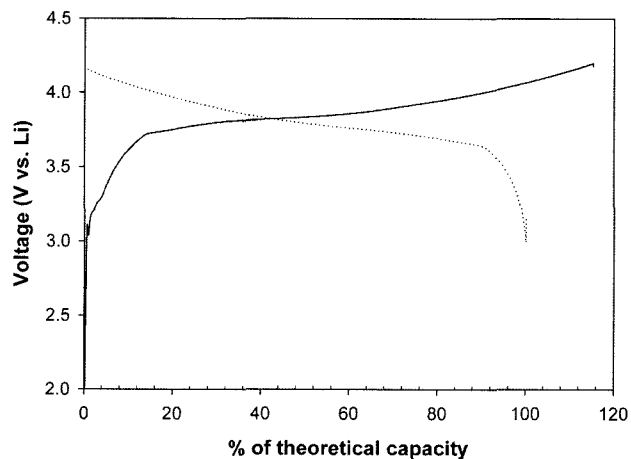


Fig. 9. Charge and discharge curves at precycling of the cell based on stretched PVC/P(VdF-co-HFP)/PMMA separators.

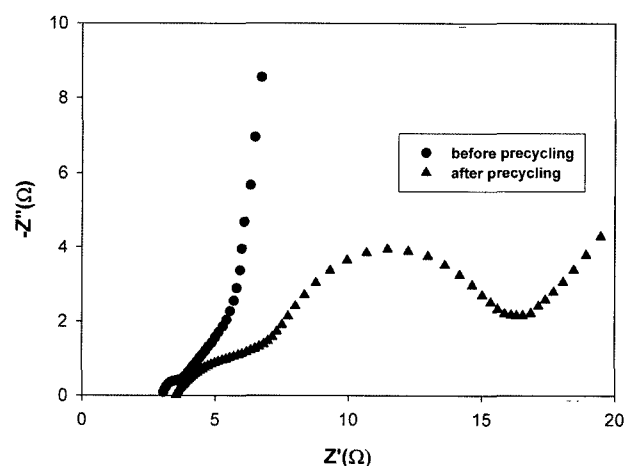


Fig. 10. A.c. impedance spectra of graphite|stretched PVC/P(VdF-co-HFP)/PMMA based electrolyte/LiCoO₂ unit cell.

remained at 99% level of the initial capacity even after 10 cycles.

The rate capability of the given cell was also examined. The

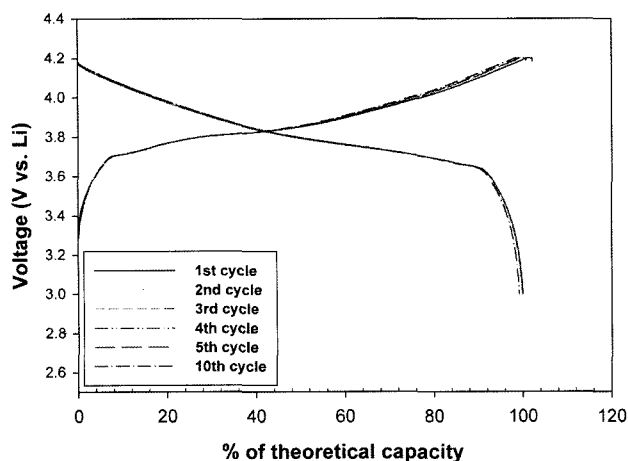


Fig. 11. Charge/discharge curves of graphite/stretched PVC/P(VdF-co-HFP)/PMMA based electrolyte/LiCoO₂ unit cell at 0.2C rate.

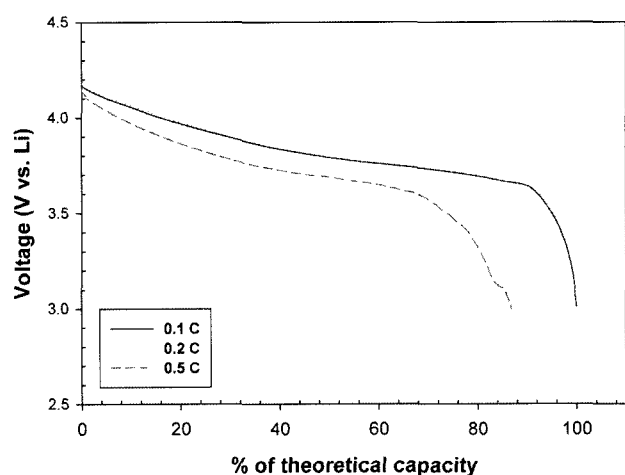


Fig. 12. Discharge curves of graphite/stretched PVC/P(VdF-co-HFP)/PMMA based electrolyte/LiCoO₂ unit cell at various discharge rates.

discharge curves obtained at different current rates are shown in Fig. 12. It was found that both the voltage and the capacity were decreased with increasing the current rate. At 0.2C rate, it shows the same discharge capacity at 0.1C rate. At higher current rate of 0.5C, the decrease of discharge capacity was very significant. This seems to attribute to low ionic conductivity of the prepared separator containing liquid electrolyte.

Conclusions

A new porous separator based on PVC/P(VdF-co-HFP)/PMMA could be prepared by phase inversion method. It could be stretched uni-axially up to 5 times of the original length at high temperature. The tensile strength and ionic conductivity are increased with increasing draw ratio. These are attributed to the enhanced the orientation of polymer chain resulting in expansion of the pores and the increased pathway connectivity. The cell based on the new separator showed a good electrochemical performance at rather a lower current rate.

Acknowledgement

This research was supported by a grant from Strategic R&D Program of Ministry of Commerce, Industry and Energy in KOREA.

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