

Short communication

Electrochemical properties and cycle performance of electrospun poly(vinylidene fluoride)-based fibrous membrane electrolytes for Li-ion polymer battery

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Abstract

Prototype cells were prepared by hot pressing of the cathode and the anode coated with poly(vinylidene fluoride-hexafluoropropylene) P(VdF-HFP) and poly(vinylidene fluoride) PVdF-based fibrous membranes, respectively. Electrochemical properties and cycle performance of them before and after hot pressing were investigated. Pressing of the fibrous membrane resulted in decrease of the apparent porosity and electrolyte uptake. The prototype cell using hot-pressed membrane electrolyte showed continuous fading of the capacity while that using non-pressing fibrous membrane almost retained the initial capacity after 100 cycles at room temperature (0.5 C rate). In the case of cycle test at 80 °C, however, the capacity was slightly decreased after the initial capacity fading of about 6.5% during the first 10 cycles due to the evaporation of liquid electrolytes. Rate performance exhibited about 97% and 72% of the full capacity at the 1 C rate and 2 C rate, respectively. The capacities at 5 C rate and 10 C rate were about 27–28% of the full capacity similarly because of the reduction of the entrapped liquid phase due to the swell of the fibrous structure. © 2006 Elsevier B.V. All rights reserved.

Keywords: Lithium ion polymer battery; Electrospinning; poly(vinylidene fluoride); Fibrous membrane electrolyte

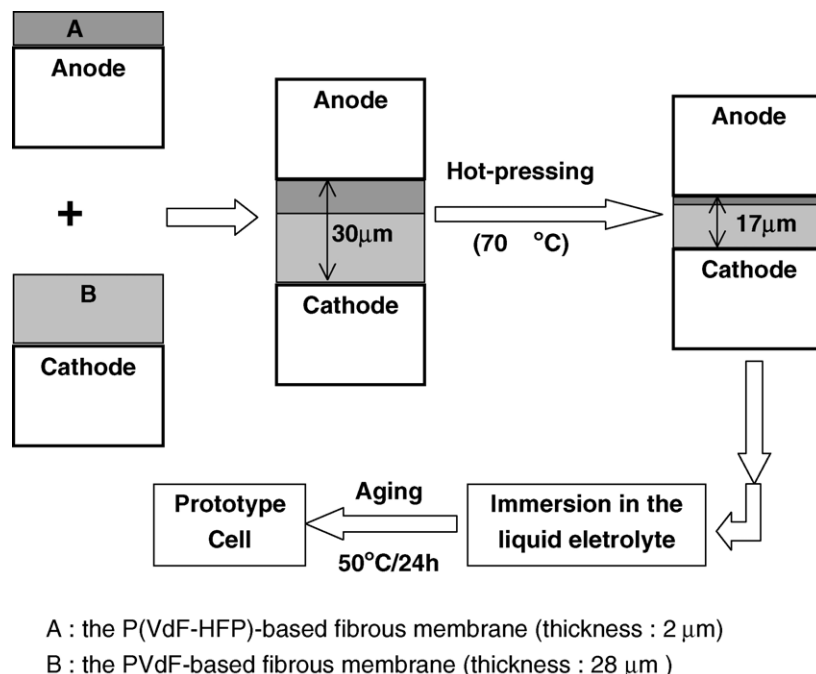
1. Introduction

Lithium ion cells are widely used for mobile electronics because of their powerful energy storage capacities. The recent efforts for the advanced lithium ion batteries have been focused on the replacement of the common liquid electrolyte with gel polymer electrolytes or fully solid polymer electrolytes conducting lithium ions to finally achieve the full plastic batteries. Gel polymer electrolyte encapsulates a large amount of liquid electrolyte in the nanoporous structure of the polymer host. As such, they show a good ionic conductivity at room temperature and a high electrochemical stability of up to the lithium ion battery operation voltage sufficient for rechargeable batteries [1,2]. They are not sufficient, however, for high-rate

performance and cycle performance due to their nanoporous structure and the flow property of gel polymer electrolytes at high temperatures. Although microporous gel electrolytes using poly(vinylidene fluoride)(PVdF) and poly(vinylidene fluoride-hexafluoropropylene) P(VdF-HFP) may overcome these disadvantages [3,4], they still showed insufficient performances [5]. Increasing the pore size in the PVdF matrix can help to enhance the ionic conductivity and thus cell rate capability. The improvements observed in the trend from gel to nanoporous to microporous PVdF based polymer electrolytes. Generally, microporous membranes, activated by soaking them in an electrolyte solution, can contain a large amount of electrolyte solution that will enable them to show good ionic conductivity and low bulk interfacial resistance [2,5].

Recently we developed new microporous polymer electrolytes composed of electrospun ultra fine fibrous polymer membranes using PVdF [6,7], P(VdF-HFP) [8], and polyacrylonitrile PAN [9]. Electrospun polymer membranes are com-

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Scheme 1. Process for preparation of prototype cell using the electrospun PVdF-based fibrous polymer electrolyte.

posed of ultra-fine fibers with diameters in the range of several micrometers to tens of nanometers [10] and have porosities in the range of 30–90% and pore sizes in the range of a few hundreds nanometers to a few micrometers. In addition, a fully interconnected open pore structure offers a good ion conduction channel and a large specific surface area. In previous study, the physical and electrochemical properties of electrospun PVdF-based polymer electrolyte were investigated because it was expected to provide more thermally stable polymer electrolytes than those of P(VdF-HFP) copolymers [6,7]. It exhibited good electrochemical stability and the interfacial resistance (R_i) between the polymer electrolyte and the lithium electrode was very low compared with those of other gel polymer electrolytes. The electrospun fibrous membrane showed a good microporous matrix of polymer electrolyte for application in lithium ion polymer batteries.

In this study, we investigated the cycle performances and the rate capabilities of electrospun PVdF-based fibrous membranes electrolyte for lithium ion polymer batteries.

2. Experimental

Electrospun fibrous membranes were prepared using 17 wt% PVdF (Kynar 761, Atofina) and 14 wt% P(VdF-HFP) copolymer (Kynar flex 2801, Atofina) solutions dissolved in the mixed solvent of acetone/*N,N*-dimethylacetamide (DMAc) (5:5 and 7:3 by weight, respectively). The P(VdF-HFP)-based fibrous membrane was deposited on a mesocarbon microbead (MCMB) anode (SKC supplied, Korea) according to the typical electrospinning method [10]. The membrane thickness was controlled at about 2 μm . The PVdF-based fibrous membrane with about 28 μm thickness was also deposited on a LiCoO₂ cathode (SKC supplied, Korea) similarly. The surface morphology of the elec-

trospun fibrous membranes was observed with a field-enhanced scanning electron microscope (FE-SEM, Hitachi-4200).

The PVdF- and P(VdF-HFP)-based fibrous membranes coated on the anode and the cathode, respectively, was sandwiched by hot pressing at 70 °C according to the Scheme 1. The thickness of electrospun fibrous membrane in the resulting cell was controlled to about 17 μm . The cells were vacuum-dried overnight at 80 °C. Dried cells were immersed in 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, w/w/w) solution (Merck) for 12 h in a glove box under argon atmosphere ($\text{H}_2\text{O} < 1\text{ppm}$). Then the cells were sealed with a polyethylene-coated aluminum pouch under vacuum and aged at 50 °C for 24 h.

An ionic conductivity cell was assembled by sandwiching a given fibrous polymer electrolyte between two stainless steel blocking electrodes (2 cm \times 2 cm) in a glove box filled with argon gas. The ionic conductivity was measured using an ac impedance method over the frequency range of 10 mHz to 1 MHz, with ac amplitude of 10 mV and a temperature range of -20 °C to 60 °C using IM6e (Zahner Elektrik Co.).

Linear sweep voltammetry was used to determine the electrochemical stability window of electrospun fibrous polymer electrolyte. The measurement was carried out using three-electrode electrochemical cell consisting of nickel working electrode and a lithium reference and counter electrode. An electrochemical analyzer (CHI, Model 600) was used under the conditions of the scan rate of 1 mV S⁻¹ and the potential range of 2–6 V versus Li⁺/Li.

The charge-discharge tests of prototype cells were conducted with a battery cycler (WBCS-3000, WonAtech Co., Korea). The cell performance was evaluated galvanostatically with a cut-off potential of 2.75 V and 4.2 V at different temperatures and different current rates (0.2 C, 0.5 C, 1 C, 2 C, 5 C, 10 C).

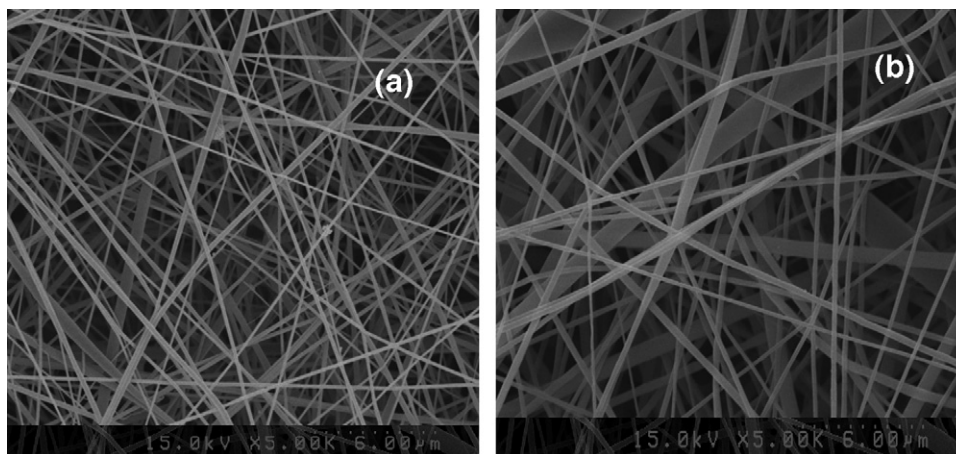


Fig. 1. SEM images of the electrospun PVdF-based fibrous membrane: (a) before hot pressing (average fiber diameter: 300 nm); and (b) after hot pressing (average fiber diameter: 420 nm).

3. Results and discussion

As shown in Scheme 1, prototype cell was prepared by hot pressing of the cathode and the anode at 70 °C. A LiCoO₂ cathode was coated with the PVdF-based fibrous membrane of about 28 μm thickness. The anode was also coated with the P(VdF-HFP)-based fibrous membrane of about 2 μm thickness to improve the adhesion between the electrode and the PVdF-based fibrous membrane. The thickness of the fibrous membrane in the prototype cell was reduced to about 17 μm after hot pressing. Fig. 1 shows SEM images of electrospun PVdF-based fibrous membrane before and after hot pressing. The fibrous membrane before hot pressing was composed of ultrafine fibers having the average diameter of about 300 nm. It shows the apparent porosity of 86% and the electrolyte uptake of 344%, respectively [8]. Its apparent porosity and electrolyte uptake after hot pressing were changed to about 80% and 279%, respectively. The apparent porosity, the electrolyte uptake and mean pore size of electrospun PVdF-based fibrous membrane greatly depend on the average fiber diameter. Smaller diameter of fiber shows higher electrolyte uptake and better relative absorption ratio (leakage behavior) [7]. Pressing of the electrospun fibrous membrane has a great effect on the apparent porosity, mean pore size as well as pore structure (tortuosity). Especially, the decrease of mean pore size by hot pressing is expected to improve electrolyte leakage behavior. Pressing of the fibrous membrane, however, resulted in decrease of the apparent porosity and electrolyte uptake.

Typical ac impedance spectra for the fibrous membrane electrolyte using blocking electrodes (SS/polymer electrolyte/SS) before and after hot pressing were obtained in the range of -20 °C to 60 °C. The conductivities (σ) were determined using the bulk resistance (R_b) in complex impedance spectra and the equation $(\sigma) = L(A)^{-1}(R_b)^{-1}$, where L is the normal thickness (~17 μm); and A , the electrode area. Fig. 2 shows the Arrhenius plots for the ionic conductivities of fibrous membrane electrolytes at different temperatures. The ionic conductivity of PVdF-based fibrous membrane, which was not pressed and contained the liquid electrolyte of 344%, was approximately

1.04 mS cm⁻¹ at 20 °C and was below 0.85 mS cm⁻¹ at 0 °C. But, the fibrous membrane of smaller fiber diameter generally showed high ionic conductivity of 1 mS cm⁻¹ at the 0 °C because of its high electrolyte uptake [7,8]. Hot-pressed fibrous membrane electrolyte containing the liquid electrolyte of about 279% shows the ionic conductivity of 1.04 mS cm⁻¹ and 0.63 mS cm⁻¹ at 20 °C and 0 °C, respectively. Decrease of ionic conductivity due to low electrolyte uptake in the hot pressed fibrous membrane might reflect poor performance on the cycle-life or high rate capability of battery.

The electrochemical stability of the fibrous polymer electrolyte before and after hot pressing was evaluated between 2.0 V and 6 V at 20 °C, as shown in Fig. 3. In general, the electrochemical stability window of a given electrolyte is established using linear sweep voltammetry of a given electrolyte, a blocking electrode and a lithium reference electrode. A decomposition process associated with electrode/electrolyte results in the onset

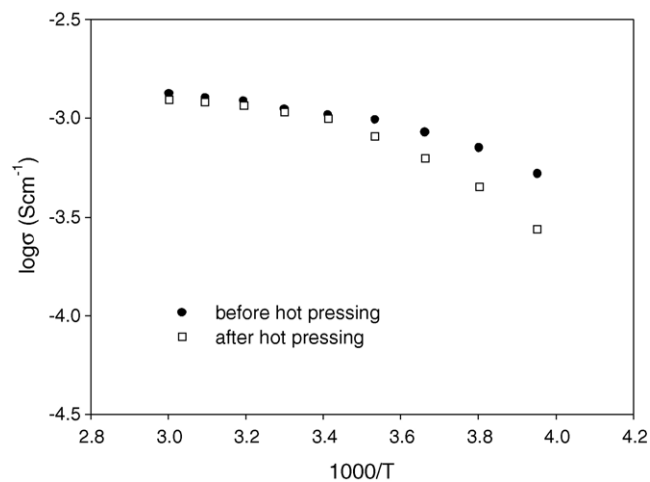


Fig. 2. The ionic conductivities of electrospun PVdF-based fibrous membranes that contained 1 M LiPF₆ in EC/DMC/DEC (1/1/1 by weight) as a function of temperature.

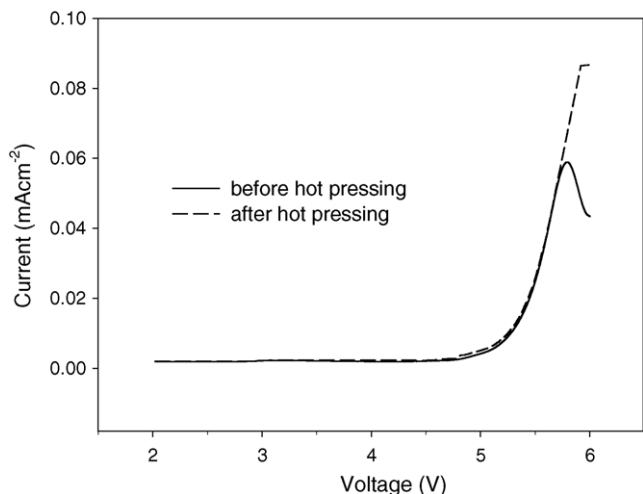


Fig. 3. The electrochemical stability windows of electrospun PVdF-based fibrous membranes that contained 1 M LiPF₆ in EC/DMC/DEC (1/1/1 by weight). (a) non-pressing; (b) hot-pressing that measured by three-electrochemical cell consisting of a nickel working electrode, a lithium reference electrode, and the count electrode (scan rate: 1 mV s⁻¹).

of the current in the high voltage range and this onset voltage is the upper limit of the electrolyte stability range [11,12]. Both of the PVdF-based fibrous polymer electrolytes containing a 1 M LiPF₆-EC/DMC/DEC (1/1/1 by weight) solution without regard to hot pressing exhibited good electrochemical stability up to above 4.7 V. The current onsets are detected around 4.7 V versus Li/Li⁺. This indicates no decomposition of any components in this potential region and is high enough to allow for the most common lithium-ion electrode couples with high voltage.

The prototype cells were subjected to a preconditioning cycles with a cut-off voltage of 4.2 V (the upper limit) and 2.7 V (the lower limit) at a constant current of 8 mA (at the 0.2 C rate) during the initial five cycles before cycle tests at higher rate. In this experiment, the theoretical capacity of our LiCoO₂ electrode was estimated to about 145 mA hg⁻¹. Fig. 4 shows the discharge capacities of the prototype cell as a function of

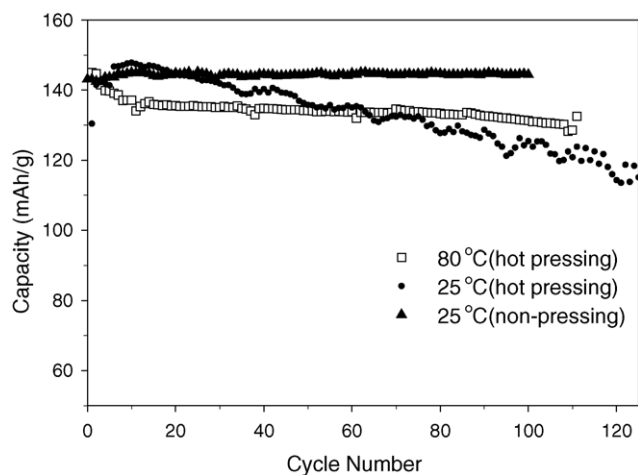


Fig. 4. The cycle performance of the prototype cell using electrospun PVdF-based fibrous membrane electrolyte at room temperature and 80 °C (at the 0.5 C rate).

cycle number at the 0.5 C rate (20 mA) and at different temperatures. The discharge capacity of prototype cell using non pressed PVdF-based fibrous membrane containing about 344% liquid electrolyte almost retained the initial capacity after 100 cycles at room temperature. Hot pressed membrane containing lower content of electrolyte solution steadily decreased at room temperature and fell below an initial capacity of about 86% after the 110 cycles and 61% (88.5 mA hg⁻¹) after the 250 cycles. The interfacial resistance of the gel polymer electrolyte generally tended to increase because of the formation of the passive layer due to the reaction between the aprotic solvents and the lithium electrodes during the long storage time [13,14]. In the previous papers [7], the interfacial resistance of the electrospun PVdF- or P(VdF-HFP)-based fibrous membranes significantly increased with the storage time. The swell of fibrous membrane by the entrapped liquid electrolyte results in not only an increase of the swollen polymer phase as the slow ion conduction path but also a reduction of the entrapped liquid phase in the pore as the high ionic conduction path. Therefore, the long storage could cause the increase in the interfacial resistance through the reduction of the electrolyte solution in the interface between the lithium electrode and the fibrous polymer electrolyte, and through the reduction of the contact area between the swollen fiber and the lithium electrode due to the expansion of the swollen fiber's diameter. The electrochemical reaction like the charge/discharge greatly enhanced the swell of nanofibers [9]. Fig. 5 showed DSC thermograms of hot pressed PVdF-based fibrous membrane electrolytes after cycle tests at room temperature. Melting points of the swollen fibrous membrane electrolytes were remarkably depressed during the cycle tests. This indicated that the cycle tests could cause the increase in internal resistance of polymer electrolyte and the interfacial resistance through the reduction of the electrolyte solution in the interface between the lithium electrode and the fibrous polymer electrolyte. So, the continuous fading of discharge capacity of hot-pressed membrane electrolyte at room temperature is assumed to be caused by deficient electrolyte in the pore structure due to swell of fibrous membrane containing lower content of liquid electrolyte (279%), compared

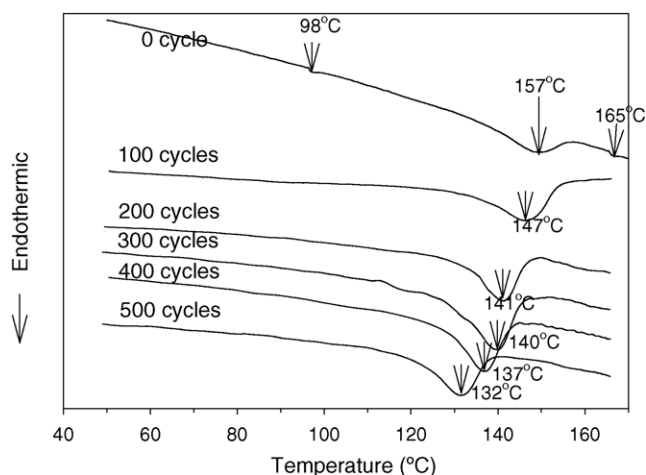


Fig. 5. DSC thermograms of hot pressed PVdF-based fibrous membrane electrolytes after cycle tests at room temperature.

to non-pressed membrane. In the case of cycle test at 80 °C, however, the capacity was slightly decreased after the initial capacity fading of about 6.5% during the first 10 cycles. The capacity fading in the first 10 cycles may be due to the evaporation of liquid electrolytes. Melting temperature of the PVdF-based fibrous membrane was depressed through swell in the liquid electrolyte. The swell of PVdF-based fibrous membrane during charge and discharge of 110 cycles at 80 °C could induce increase of its solubility in liquid electrolyte and the formation of more homogeneous gel membrane, resulting in excellent cycle-life. Fig. 4 also showed different capacities, compared to those of the prototype cells using the same cathode, the same anode, and the same liquid electrolyte, but using PVdF nanofibrous membrane electrolyte [7] and PVdF-HFP nanofibrous membrane electrolyte [8]. Solvent molecules have been known to cointercalate as the associated form of Li⁺ into graphite layers during charging [15,16]. The cointercalated solvent molecules were not easily released from the graphite electrode, and were transformed into inactive materials that formed a passivation layer during their charge/discharge performances. So, the capacities of the cells using the same cathode, the same anode, and the same nanofibrous membrane were greatly affected by the solvent composition of liquid electrolyte [9]. Swelling of fibrous membranes by liquid electrolyte is also greatly influenced by a kind of polymer materials. At present, the origin of different capacities is not clear. But differences of swelling of fibrous membranes by liquid electrolyte may have effect on formation of cointercalation as the associated form of Li⁺ and then reflect on the different capacities by a kind of fibrous polymer electrolyte membranes.

The rate dependency was also investigated. Fig. 6 shows the discharge profiles of prototype cells using hot-pressed PVdF-based fibrous membrane electrolyte as a function of discharge rate. In the view of a voltage plateau at about 3.7 V versus Li/Li⁺ due to the intercalation of Li⁺ into LiCoO₂, prototype cells using the hot pressed PVdF-based fibrous membrane electrolyte showed very good cycle performance between 3.0 V and 4.2 V. The theoretical capacity of our LiCoO₂ electrode at 0.2 C rates

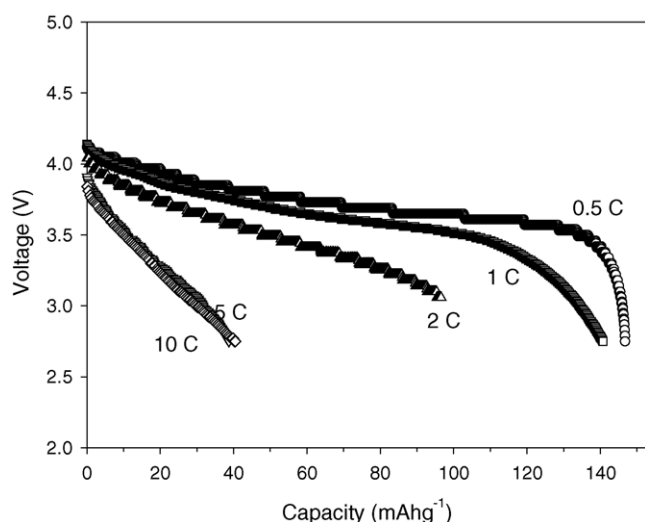


Fig. 6. Discharge curves of the prototype cell using the hot pressed PVdF-based fibrous membrane electrolyte as a function of C rate.

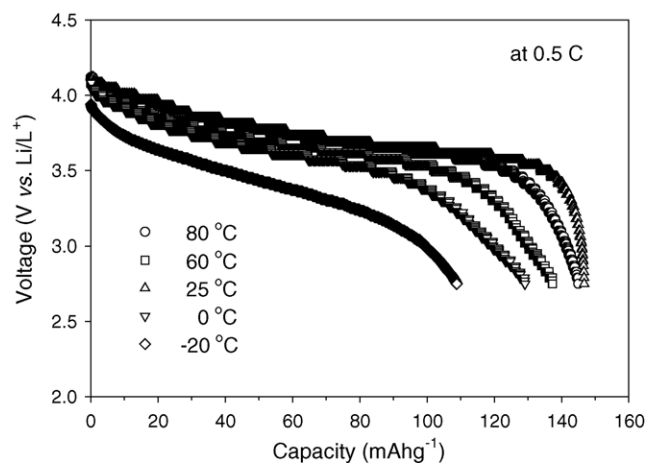


Fig. 7. Discharge curves of the prototype cell using the hot pressed PVdF-based fibrous membrane electrolyte at different temperatures.

was estimated to about 145 mA hg⁻¹, indicating 100% capacities. This cell exhibited about 97% (141 mA hg⁻¹) and 72% (105 mA hg⁻¹) of the full capacity at the 1 C rate and 2 C rate, respectively. The capacities at 5 C rate and 10 C rate were about 27–28% of the full capacity similarly. The reduced capacity at high rate is known to be due to the low value of the chemical diffusion coefficient of Li⁺ in the LiCoO₂ lattice and the lower diffusion rate of Li⁺ in gel polymer electrolyte, as compared with that in liquid electrolyte [17]. The entrapped liquid electrolyte in a fully interconnected microporous structure partially penetrated the fibrous structure, resulting in an increase of the swollen polymer phase as the slow ion conduction path. It gave not only an increase of ionic conductivity, electrochemical stability and electrolyte retention ability, but also a reduction of the entrapped liquid phase in the pore as the high ionic conduction path. Therefore, the swell of the fibrous structure as the slow ion conduction path and the reduction of the entrapped liquid phase might bring on the decrease of the discharge capacity at the high rate.

Fig. 7 showed discharge curves of the prototype cell using the hot pressed PVdF-based fibrous membrane electrolyte at different temperatures. The prototype cells retained 90% and 76% of the room temperature capacity at 0 °C and -20 °C, respectively. In the case of 60 °C and 80 °C, however, they showed 96% and 99% of the room temperature capacity, respectively. The temperature dependence of capacity might be caused by solvent viscosity at lower temperature and the swell of fibrous membrane at higher temperature.

4. Conclusions

Pressing of the fibrous membrane resulted in decrease of the apparent porosity and electrolyte uptake. The discharge capacity of prototype cell using the non-pressing fibrous membrane almost retained the initial capacity after 100 cycles at room temperature (0.5 C rate). The prototype cell using hot-pressed membrane electrolyte showed continuous fading of the capacity because of deficiency of liquid electrolyte in the pore structure due to swell of fibrous membrane containing lower content of

liquid electrolyte compared to non-pressed membrane. In the case of cycle test at 80 °C, however, the capacity was slightly decreased after the initial capacity fading of about 6.5% during the first 10 cycles due to the evaporation of liquid electrolytes. The swell of PVdF-based fibrous membrane during 110 cycles at 80 °C could induce increase of its solubility in liquid electrolyte and the formation of more homogeneous gel membrane, resulting in excellent cycle-life.

Rate performance of the prototype cell exhibited about 97% and 72% of the full capacity at the 1 C rate and 2 C rate, respectively. The capacities at 5 C rate and 10 C rate were about 27–28% of the full capacity similarly. The swell of the fibrous structure as the slow ion conduction path and the reduction of the entrapped liquid phase might bring on the decrease of the discharge capacity at the high rate.

The temperature dependence of capacity might be caused by solvent viscosity and the swell of fibrous membrane at lower and higher temperature, respectively.

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