

Novel porous separator based on PVdF and PE non-woven matrix for rechargeable lithium batteries

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Abstract

The novel porous separator based on PVdF (poly(vinylidene fluoride)) and a PE (polyethylene) non-woven matrix is prepared by coating PVdF/NMP solution on the matrix (NMP: *N*-methyl-2-pyrrolidone). The pore structure is generated in the PVdF region by phase inversion of the polymer solution. The PE non-woven matrix imparts mechanical strength and a thermal shut-down property to the separator, while the PVdF component provides a hydrophilic ionic conducting phase. The physical properties of the separator, such as morphology, pore size and its distribution, porosity and mechanical strength, are measured. The ionic conductivity of the separator is $8.9 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C. The capacity at the C/2 rate is maintained at about 86% of the initial value on the 100th cycle at the room temperature. The electrolyte is stable up to 4.5 V in the presence of the novel separator.

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1. Introduction

The separator plays an important role in rechargeable lithium batteries, namely, as an electrical insulator and an ionic conductor between the anode and the cathode. Generally, polyethylene(PE)-based separators have been used in conventional lithium batteries. The PE separators have good mechanical properties, and also they can effectively prevent thermal runaway that results from short-circuits or rapid overcharging of the battery. On the other hand, they exhibit poor compatibility with liquid electrolytes due to their hydrophobic property, and their manufacturing cost is high. Many studies of coating PE separators with gel electrolyte have been undertaken to enhance their compatibility with liquid electrolytes [1–6]. These modified separators show

good mechanical strengths and a good thermal shut-down property, as well as compatibility with the liquid electrolyte. Nevertheless, the cost of the PE separators is still high. Some research groups have tried to develop novel porous separators prepared from non-polyolefin materials for rechargeable lithium batteries [7,8]. Kuribayashi [7] made a composite cellulosic separator that was composed of fine fibrillia cellulosic fibres embedded in a microporous cellulosic film. Prosimi et al. [8] used a PVdF–HFP polymer matrix with inorganic fillers to form porous separators. They could not, however, succeed in completely satisfying the requirements of separators.

In this work, a novel microporous separator based on PVdF and a PE non-woven matrix is prepared. The PE matrix can lead to a low-cost separator with good mechanical strength and a thermal shut-down property. The PVdF matrix can enhance the compatibility with the liquid electrolyte. The pore structure is generated in the PVdF phase through

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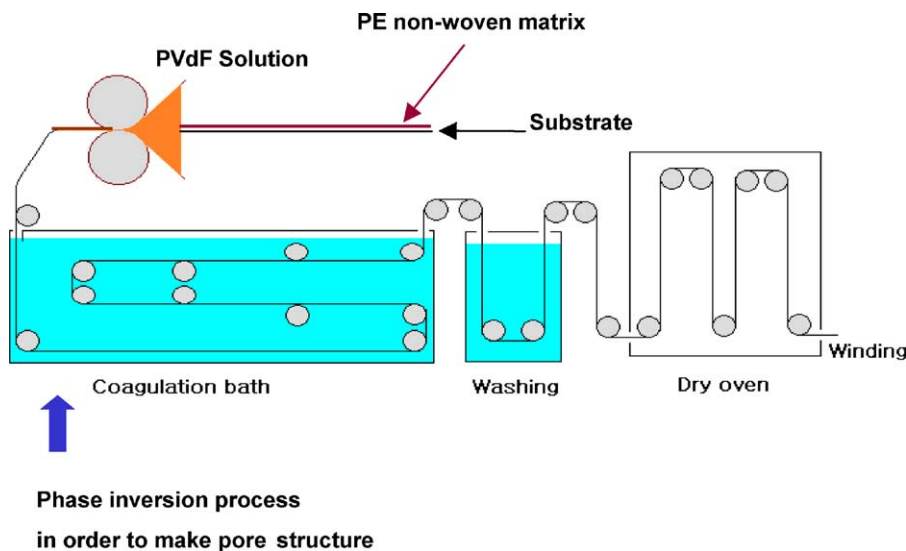


Fig. 1. Preparation of porous separator based on PVdF and PE non-woven matrix.

a phase-inversion process. The physical and electrochemical characteristics of this novel microporous separator are presented.

2. Experimental

2.1. Preparation of porous separator

The porous separator was prepared by coating PVdF/NMP solution on a non-woven matrix that was carried on a polyethylene terephthalate (PET) substrate, as shown in Fig. 1. The required amount PVdF (Solvay) of weight-average molecular weight 600,000 was dissolved in *N*-methyl-2-pyrrolidone (NMP, Aldrich). The viscosity of the polymer solution was measured at 20 °C using a cone and plate viscometer. Prior to coating with PVdF, the PE non-woven matrix was roll-pressed in order to reduce its thickness from 55–60 μm to about 20 μm. The coated PE non-woven matrix was then passed through a coagulation bath that was filled with distilled water. Demixing of the polymer solution took place in the water coagulation bath at 30 °C, and thereby a pore structure in the PVdF was generated. The separator was washed with distilled water and dried at 160 °C to remove the residual solvent.

2.2. Measurement of physical properties of separator

The morphology of the separator was investigated by means of scanning electron microscopy (SEM, JEOL 5360). The specimens for the SEM images of the cross-section of the separators were prepared by fracturing the corresponding film in liquid nitrogen. The pore-size distribution and porosity of the specimens were 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 , the applied pressure; γ , the surface tension of mercury and ψ , the contact angle of mercury. The mechanical strength of the separator was characterized in terms of tensile properties and elongation ratio by using an AFG 500N (Mecmesin) tester according to KS M 3054. The tensile rate was controlled at 50 mm min⁻¹.

The thermal behaviour of the separator was studied by using a differential scanning calorimeter (DuPont TA 2100 DSC). This was scanned from –80 to 200 °C by heating at a rate of 10 °C per min under a nitrogen atmosphere.

Table 1
Physical properties of novel separator

| | Unit | Value | Method |
|--------------------------|--------------------------------|-------|---------------------|
| Thickness | μm | 33 | Micrometer |
| Porosity | % | 53 | Mercury porosimeter |
| Average pore size | μm | 0.035 | Mercury porosimeter |
| Total instruction volume | mL g ⁻¹ | 0.784 | Mercury porosimeter |
| Total pore area | m ² g ⁻¹ | 90.1 | Mercury porosimeter |
| Tensile strength | MD: kgf cm ⁻² | 271 | KS M 3054 |
| | TD: kgf cm ⁻² | 119 | KS M 3054 |
| Elongation ratio | MD: % | 74 | KS M 3054 |
| | TD: % | 57 | KS M 3054 |

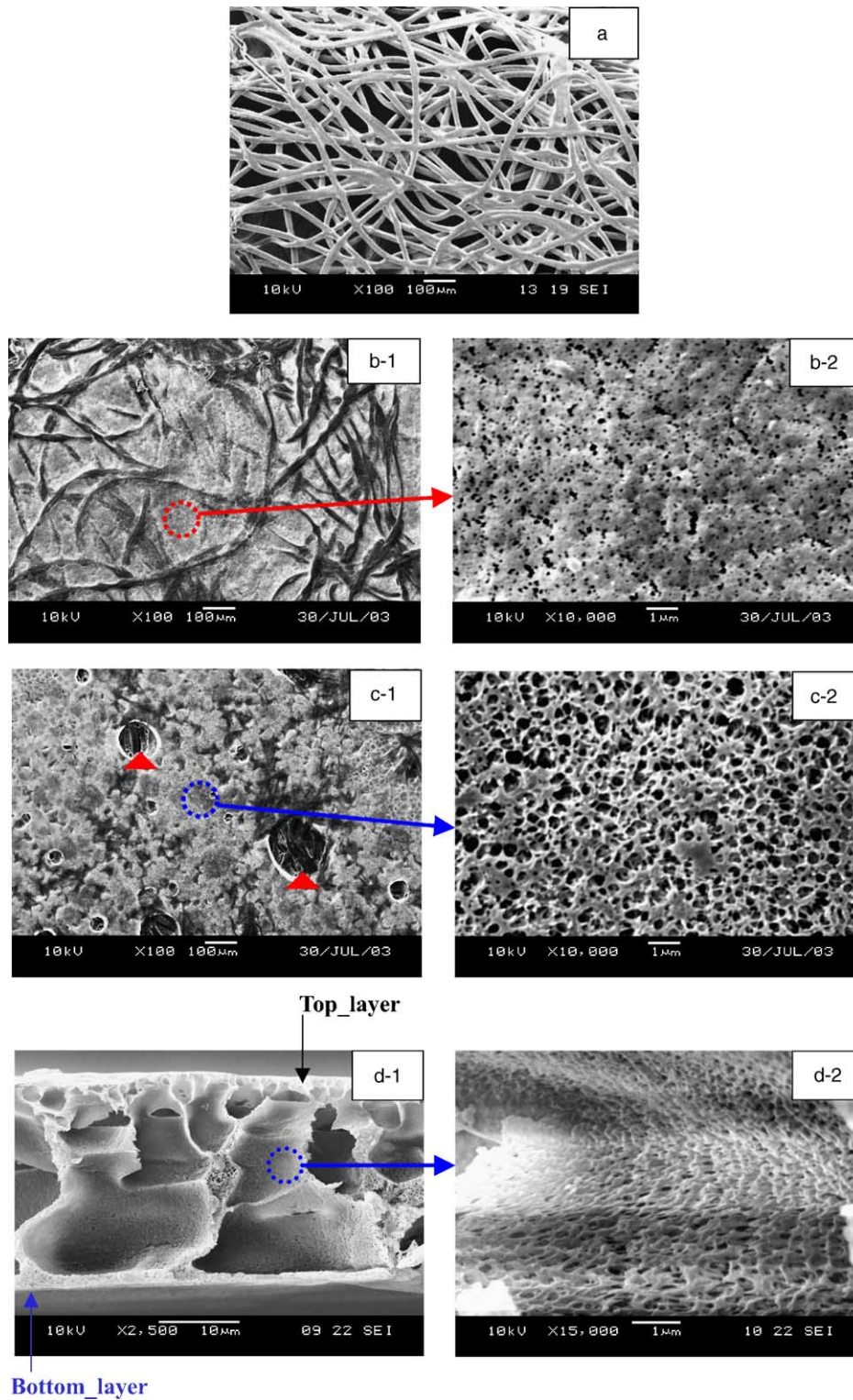


Fig. 2. Scanning electron micrographs of PE non-woven matrix and porous separator based on PVdF and PE non-woven. (a) PE non-woven; (b) surface morphology (top layer) of separator [b-1: $\times 100$; b-2: $\times 10,000$]; (c) surface morphology (bottom layer) of separator [c-1: $\times 100$; c-2: $\times 10,000$]; (d) cross-section morphology of separator [d-1: $\times 2500$; d-2: $\times 15,000$].

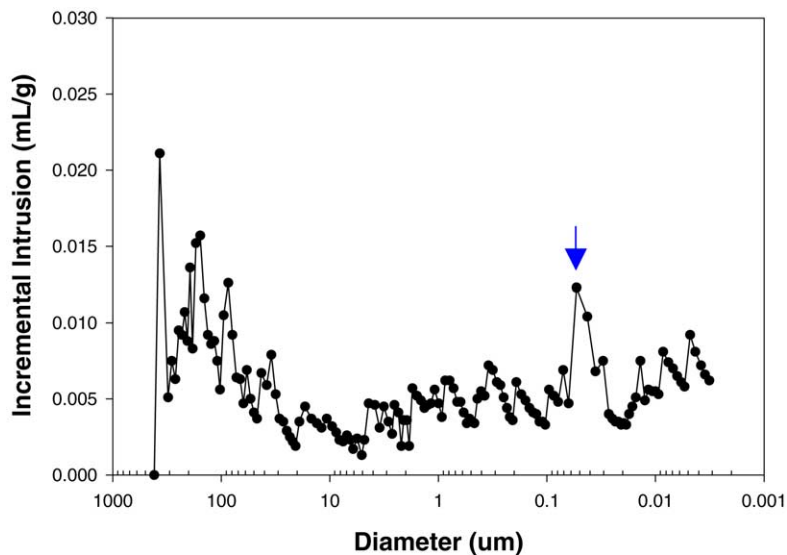


Fig. 3. Pore-size distribution of novel separator.

2.3. Preparation of electrodes

The carbon anode was prepared with doctor blade by coating an NMP slurry of 95 wt.% graphitized mesocarbon microbeads (MCMB2528) and 5 wt.% PVdF(Kynar 741) as a binder material on a copper foil. The cathode slurry contained 88 wt.% LiCoO₂, 6.8 wt.% super-P and 5.2 wt.% poly(vinylidene fluoride) in NMP and was cast on aluminum foil. The thickness of the cathode was about 90 μm. The dried electrodes were roll-pressed to enhance both particle contact and adhesion to the foils. Both the cathode and the anode were immersed in liquid electrolyte before cell assembly to fill the pores in the electrodes with liquid electrolyte.

2.4. Electrical measurements

The separators, immersed in liquid electrolyte, namely, 1M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC)/propylene carbonate (PC) [35/60/5, by wt.] (Samsung Cheil Industries, Korea), were sandwiched between the two stainless-steel (SS) electrodes. The ionic conductivities were obtained from the 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. A PE separator (thickness = 20 μm, porosity = 70%) was used as a reference for comparison. The impedance of a unit cell of configuration LiCoO₂ cathode |(electrolyte based on the separator)| carbon anode was also measured.

The unit cell was assembled by sandwiching the separator after soaking in the liquid electrolyte between carbon anode and LiCoO₂ cathode. The cell (2 cm × 2 cm) was then sealed in an aluminized polyethylene bag. All assemblies of the cells were carried out in a glove box that was filled with

argon. The unit cell was typically cycled between 2.7 V and 4.2 V at a constant current density at room temperature using a TOSCAT-3000U instrument (Toyo System Co. Ltd.). The charge process was cut-off at 20% of the initial constant current.

Linear sweep voltammetry experiments were performed on a SS working electrode with lithium as both the counter and the reference electrode at a scanning rate of 2.0 mV s⁻¹.

3. Results and discussion

3.1. Physical properties of the separator

The physical properties of the novel porous separator are summarized in Table 1. The thickness of the prepared separator was 33 ± 1 μm, which is a little larger than that of conventional PE separators used in rechargeable lithium batteries.

The novel separator has an asymmetrical surface morphology, as shown in Fig. 2(b) and (c). It is clearly observed in Fig. 2(b) that the PE non-woven matrix is solidified near the top layer during the solvent–nonsolvent exchange process in the coagulation bath. This is because the density of the PE non-woven matrix (≈0.92 g cm⁻³) is lower than that of PVdF (≈1.70 g cm⁻³) and NMP/water (≈1.00 g cm⁻³). The average pore size on the surface of the top layer is about tens of nanometers. There is no PE non-woven matrix on the bottom layer surface, as shown in Fig. 2(c). Macrovoids on the bottom layer surface that result from entrapped air bubbles during the coating process due to the high viscosity of the PVdF/NMP solution, are sparsely observed. The size of the micropores on the bottom layer surface is larger than that on the top layer surface. Larger macropores are also found in the interior of

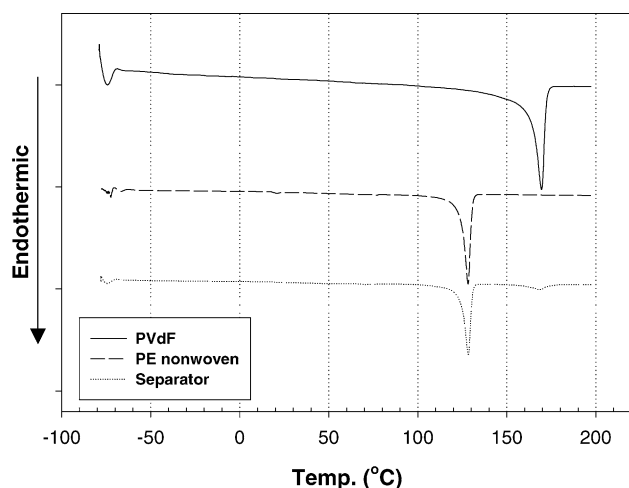


Fig. 4. DSC thermogram of novel porous separator.

the bottom layer, as shown in Fig. 2(d). This is common in phase-inversion systems using solvent–nonsolvent pairs with high mutual affinity, such as NMP/water [9,10].

The pore size, pore-size distribution, and porosity of the separator are also summarized in Table 1. The average pore size is 35 nm and the porosity is 53%. These values are in the range required for the separators of rechargeable lithium batteries. Commercial separators usually have average pore sizes in the range of 30–120 nm and porosities of 30–60% [11]. The pore-size distribution of the separator, given in Fig. 3, ranges from a few nanometers to hundreds of micrometers.

The mechanical strength (271 kgf cm^{-2}) of the separator is highly enhanced compared with non-polyolefin-based separators prepared through the phase-inversion process [6,7]. It is not, however, as high as the values obtained from conventional commercial separators due to the lower mechanical properties of the PE non-woven matrix and the many macropores in the PVdF phase. As shown in Table 1, the tensile strength for break in the machine (stretching) direction (271 kgf cm^{-2}) is higher than that in the transverse direction (119 kgf cm^{-2}). This anisotropy in the mechanical properties of the separator is basically attributed to the presence of the PE non-woven matrix.

3.2. Thermal properties of the separator

The PE non-woven matrix is expected to provide the separator with a good thermal shut-down property. Fig. 4 shows the DSC thermograms of PVdF, PE non-woven matrix, and the novel separator. PVdF and PE non-woven matrix show endothermic peaks at 169 and 128 °C, which are attributed to their melting. The melting temperature and crystallinity of the PE non-woven matrix is almost maintained in the separator. This means that the prepared separator is sufficiently effective for shutting down the operation of the cells under thermal runaway conditions. By contrast, the crystallinity of PVdF is significantly reduced

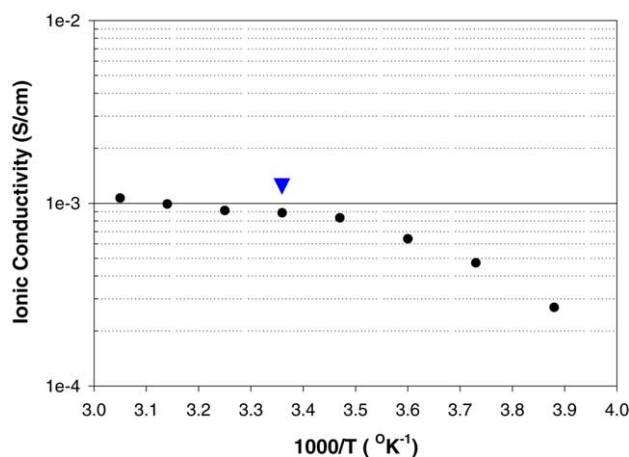


Fig. 5. Ion conductivities of electrolyte in porous separator based on PVdF and PE non-woven matrix as a function of temperature.

compared with that of pure PVdF during the phase-inversion process.

3.3. Electrochemical properties of the separator

An Arrhenius plot of ionic conductivities for the separator soaked in 1M LiPF_6 in EC/DEC/PC (35/60/5, by wt.) is shown in Fig. 5. The ion conductivity of the separator reaches $8.9 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C, which is higher than that of the PE separator (thickness = 20 μm and porosity = 70%) at room temperature ($5.8 \times 10^{-4} \text{ S cm}^{-1}$). This enhancement of ion conductivity is closely related to the uptake of liquid electrolyte into the separator. The uptake amount is determined by the following relation:

$$\text{Uptake amount (\%)} = \frac{W - W_0}{W_0} \times 100$$

where W and W_0 are the weights of the wet and dried separator, respectively. As shown in Table 2, the uptake per matrix weight in the porous PVdF phase is twice that of the porous PE phase. This indicates that there is a larger amount of liquid electrolyte in the ionic conducting phase in the novel separator.

Unit cells were subjected to a pre-conditioning cycle, with a cut-off voltage of 4.2 V for the upper limit and 2.7 V for the lower limit, at a constant current of 0.24 mA cm^{-2} (C/10 rate) before repeated charge and discharge at a higher rate. When charge–discharge cycles are performed at the C/2 rate, nearly 100% of coulombic efficiency can be achieved, as

Table 2

Uptake amount of liquid electrolyte by novel separator and conventional PE separator

| | Uptake amount in porous phase* (wt.%) | Ion conductivity (mS cm^{-1}) |
|-------------------|---------------------------------------|--|
| PVdF/PE separator | 290 | 0.89 |
| PE separator | 166 | 0.58 |

* Uptake amount into the porous phase of the separator (50 wt.% PVdF phase in novel separator).

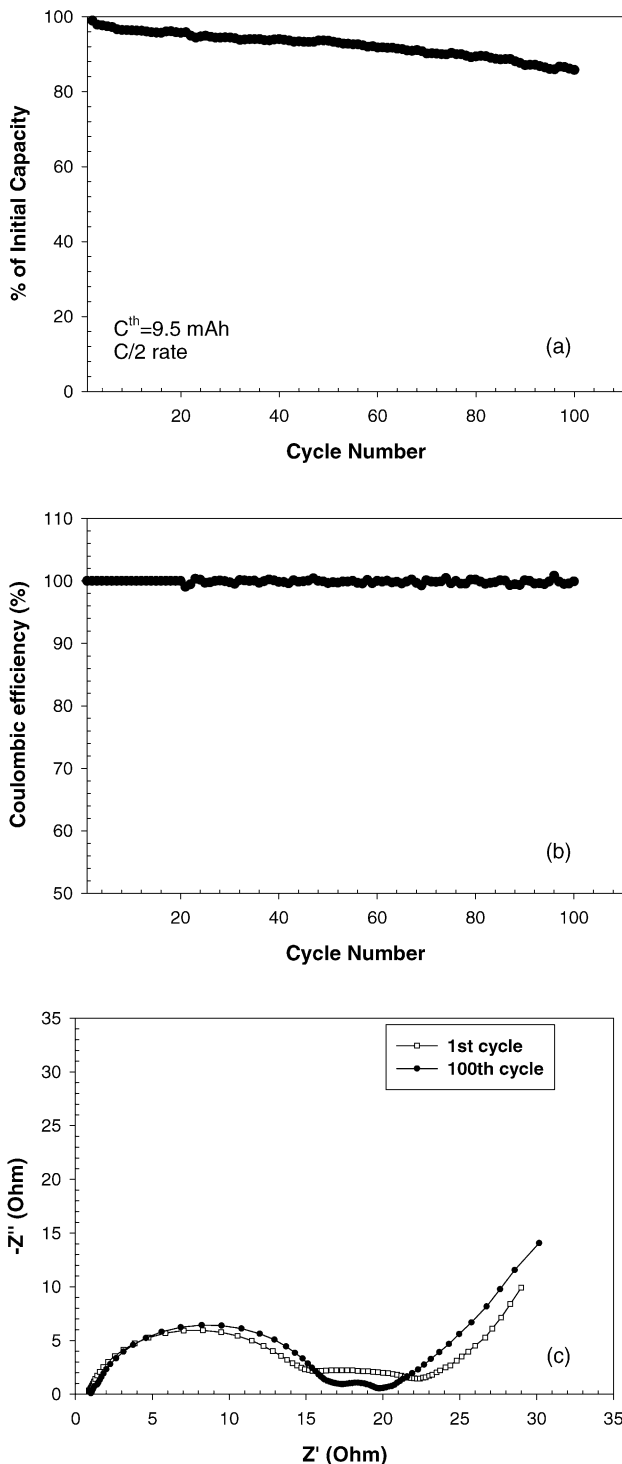


Fig. 6. (a) Charge–discharge capacity as function of cycle number of carbon|porous separator|LiCoO₂ unit cell at room temperature and discharge at $C/2$ (1.19 mA cm^{-2}) (liquid electrolyte, 1M LiPF₆ in EC/DEC/PC = 35/60/5, by wt.%); (b) coulombic efficiency as function of cycle number; (c) a.c. impedance spectra of unit cell on 1st and 100th cycle.

demonstrated in Fig. 6 (b). This is indicative of the good capacity retention of rechargeable lithium batteries that use the novel separator. The charge and discharge capacities are presented in Fig. 6(a) as a function of cycle number at the

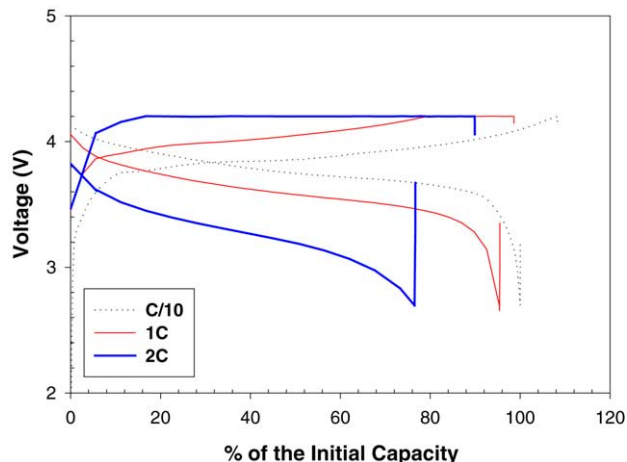


Fig. 7. Charge–discharge curves at various discharge rates for unit cell.

$C/2$ rate and with constant-current/constant-voltage charging. The discharge capacity is about 86% of the initial value on the 100th cycle. It is also found that the total resistance of the unit cell remains almost constant even after 100 cycles, as indicated in Fig. 6(c).

The charge–discharge behaviour at different rates ($C/10$, 1C, 2C) of a unit cell with the novel separator is presented in Fig. 7. Both the voltage and the capacity gradually decrease with increasing current rate. The large polarization at the 2C rate results in a reduction in the capacity to 77% of the initial discharge capacity at $C/10$. The cell shows a reasonable performance at the 1C rate (2.5 mA cm^{-2}), i.e., 96% initial capacity at the $C/10$ rate.

The electrochemical stability of the novel separator has also to be evaluated by linear sweep voltammetry. In the presence of the novel separator, the electrolyte is found to be stable up to 4.5 V as shown in Fig. 8.

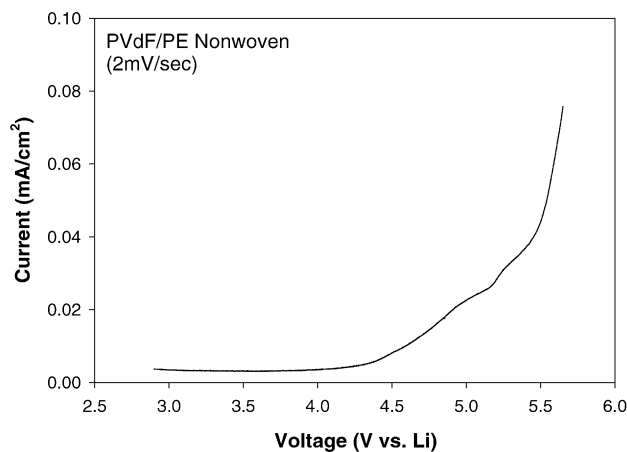


Fig. 8. Current–voltage response of novel porous separator at room temperature on a stainless-steel electrode as a working electrode (scan rate: 2 mV s^{-1}).

4. Conclusions

A novel separator based on PVdF and a PE non-woven matrix has been successfully prepared by coating PVdF on the surface of the PE non-woven matrix. The high ion conductivity of the new separator is achieved through a high uptake of liquid electrolyte in the pores of the ion conduction phase. The performance of cells with the novel separator is quite good at a reasonable discharge rate ($C/2$). It suggests that this novel separator can be a possible candidate of the economic separator for rechargeable lithium batteries.

Acknowledgement

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