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Short communication

Cycling performance of lithium-ion batteries assembled with a hybrid composite membrane prepared by an electrospinning method

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ABSTRACT

A hybrid composite membrane is prepared by electrospinning poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) copolymer and Al_2O_3 powder with a microfibrous form on both sides of a polyethylene membrane. The composite membrane shows better thermal stability and wettability for liquid electrolyte solution than polyethylene membrane. The lithium-ion cell assembled with the composite membrane exhibits good capacity retention and high rate performance due to the effective encapsulation of the electrolyte solution in the cell and the adhesive properties of the swollen polymer towards electrodes. The hybrid composite membrane prepared by the electrospinning method is expected to be a separator with enhanced thermal stability and good cycling performance for application in lithium-ion batteries.

1. Introduction

Rechargeable lithium-ion polymer batteries are being developed and produced as power sources for portable electronic devices and hybrid electric vehicles due to their high energy density and enhanced safety. In these batteries, a polymer electrolyte is an important material to achieve good battery performance such as cycle life, energy density, high rate capability and safety. To date, attempts to obtain gel polymer electrolytes consisting of matrix polymer and organic liquid electrolyte have only produced materials with poor mechanical strength, even though they exhibit high ionic conductivities in excess of $10^{-3}\,S\,cm^{-1}$ at ambient temperature [1]. In order to overcome the mechanical strength problems, microporous polyolefin membranes or porous non-woven fabrics impregnated with gel polymer electrolyte have been developed [2–11]. Such polymer electrolytes reinforced by polyolefin membranes or non-woven fabrics exhibit excellent mechanical strength for the fabrication of cells and therefore, may help to reduce the overall thickness of the electrolyte when compared to gel polymer electrolytes.

With the aim of developing highly conductive and thermally stable electrolyte material that can be handled similarly to conventional separators used in lithium-ion batteries, we prepared microporous polyethylene (PE) membrane-based hybrid composite membranes *via* electrospinning method. Electrospinning is a novel and efficient method to prepare ultrafine fibers with diameters in the range of tens of nanometers to several micrometers [12–14]. In this work, electrospinning was applied to coat microfibers with a thickness of 2–4 μm onto both sides of a PE membrane. The electrospun fibers consist of inorganic ceramic filler dispersed in polymer, which is expected to improve the thermal stability of the PE membrane and the retention capacity of liquid electrolytes. It was considered that addition of an inert ceramic filler such as aluminum oxide could prevent dimensional changes by thermal deformation at high temperature because of the frame structure of the heat-resistant ceramic powder, as many groups previously reported [15–17]. With these hybrid composite membranes, we assembled lithium-ion batteries composed of a carbon anode and a $LiCoO_2$ cathode. The cycling performances of cells with composite membranes were evaluated and compared to cells prepared with a PE membrane.

2. Experimental

2.1. Preparation of the hybrid composite membrane

Poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) (P(VdF-*co*-CTFE), Solef 32008, Solvay Co.) was used to make electrospun fiber on the PE membrane because of its good electrochemical properties and adhesion to electrodes. Aluminum oxide powder treated with octylsilane and with a particle size of 13 nm (Aeroxide Alu C 805, Evonik Industries) was used as the ceramic filler. P(VdF-

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co-CTFE) and Al_2O_3 powder (95:5 by weight) were dissolved in a mixed solvent of acetone/*N*,*N*-dimethylacetamide (DMAc) (6:4 by volume) and the resultant polymer solution was ball-milled for 24 h. Electrospun fiber was prepared and coated on the PE substrate using a typical electrospinning method [18–20]. The polymer solution was fed with a syringe pump and high voltage using a power supply was applied to the very thin tip of a nozzle connected to a syringe. When the applied electric voltage overcomes the surface tension of the polymer solution, the polymer solution is ejected from the tip of the nozzle and the polymer fibers form on the surface of the PE membrane having a thickness of 20 μm and a porosity of 49%. The thickness of the hybrid composite membrane including PE membrane substrate was controlled at 25 μm.

2.2. Electrode preparation and cell assembly

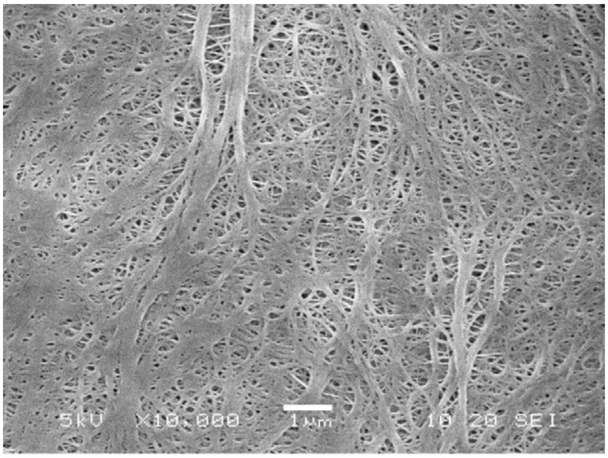
The cathode consists of 85 wt% $LiCoO_2$ (Nippon Chemical Co.), 7.5 wt% PVdF (KF-1100 Kureha), and 7.5 wt% super-P (MMM Co.). The slurry of these materials was prepared in *N*-methyl pyrrolidone (NMP) and coated on Al foil. Its active mass loading corresponds to a capacity of about 1.0 mAh cm^{-2}. The anode was also prepared by coating a NMP-based slurry of mesocarbon microbeads (MCMB, Osaka gas), PVdF, and super-P carbon (85:7.5:7.5 by weight) on copper foil. The electrodes were roll pressed to enhance particulate contact and adhesion to the current collector. Lithium-ion cells were assembled by sandwiching the composite membrane between the carbon anode and the $LiCoO_2$ cathode (geometric electrode area of 30 cm^2). The cell was then enclosed in a pouch bag injected with the electrolyte solution. The electrolyte used was 1.15 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (3:7 by volume) containing 1.0 wt% vinyl carbonate (VC) (Techno Semichem Co. Ltd.). VC was added to the liquid electrolyte as a solid electrolyte interphase (SEI) forming agent. All cells were assembled in a dry box filled with argon gas.

2.3. Measurements

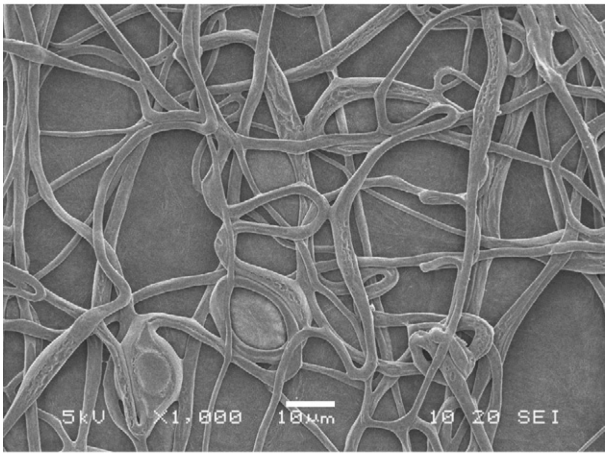
The surface morphologies of the PE membrane and hybrid composite membrane were examined using a scanning electron microscope (JEOL, JSM-6300). The thermal shrinkage of the composite membrane was measured as the dimensional change before and after being held at 105 °C for 1 h. In order to measure electrolyte uptake and ionic conductivity, the membrane was immersed in liquid electrolyte for 1 h. Following immersion, the membrane was taken out of the electrolyte solution and the excess electrolyte solution on the surface of the separator was wiped off with filter paper. The uptake of electrolyte solution was determined using the following relationship [10,20–22].

$$\text{uptake}\,(\%) = \frac{W - W_o}{W_o} \times 100$$

Here, W_o and W are the weights of the composite membrane before and after soaking in the liquid electrolyte, respectively. We measured the uptake of at least five samples in order to obtain reproducible results. The gelled membrane was sandwiched between two stainless steel (SS) electrodes for conductivity measurements. AC impedance measurements using an impedance analyzer over the frequency range of 10–100 kHz with an amplitude of 10 mV were performed to measure the ionic conductivity and interfacial resistance. The charge and discharge cycling tests of the lithium-ion cells were conducted over a voltage range of 3.0–4.2 V galvanostatically with battery test equipment at a constant current with a 0.5*C* rate.



(a) PE membrane



(b) composite membrane

Fig. 1. Scanning electron micrographs of the surfaces of (a) the porous PE membrane and (b) the hybrid composite membrane.

3. Results and discussion

Fig. 1 shows SEM images of the porous PE membrane and the hybrid composite membrane prepared by the electrospinning method. The PE membrane has a uniformly interconnected porous structure. For the hybrid composite membrane, the electrospun fibers with diameters of 2–4 μm were randomly coated on the porous PE membrane, as seen in Fig. 1(b). The presence of electrospun fibers consisting of P(VdF-*co*-CTFE) and Al_2O_3 powder improves the thermal stability of the PE membrane and also leads to efficient gelation by the liquid electrolyte when it is immersed in an electrolyte solution.

The uptake of an electrolyte solution in the composite membrane and the ionic conductivity after soaking in the liquid electrolyte (1.15 M $LiPF_6$-EC/DEC/VC) were measured and are summarized in Table 1. For comparison, the microporous PE membrane was soaked in the same electrolyte solution and the experimental data are also given in Table 1. It was found that the amount

Table 1
Physical properties of the PE and hybrid composite membranes.

	PE membrane	Hybrid composite membrane
Thickness (μm)	20	25
Uptake (%)	160	219
Ionic conductivity (S cm^{-1})	4.0×10^{-4}	5.7×10^{-4}
Thermal shrinkage (%)	3.7	2.2

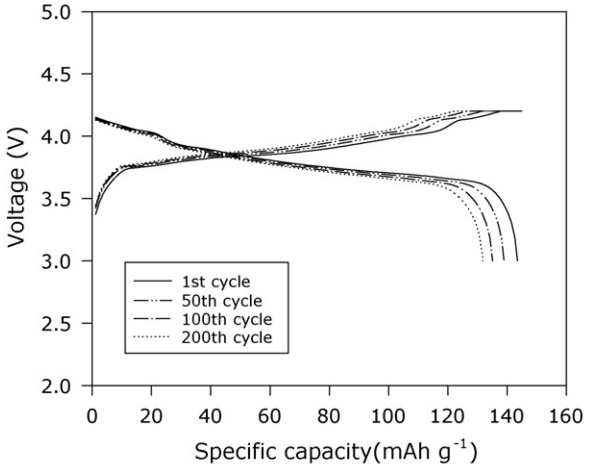


Fig. 2. Charge and discharge curves of the lithium-ion cell assembled with the hybrid composite membrane (0.5 C CC and CV charge, 0.5 C CC discharge, cut-off: 3.0–4.2 V).

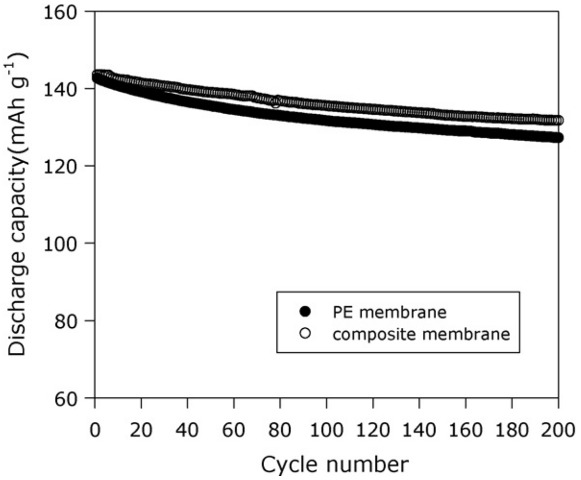


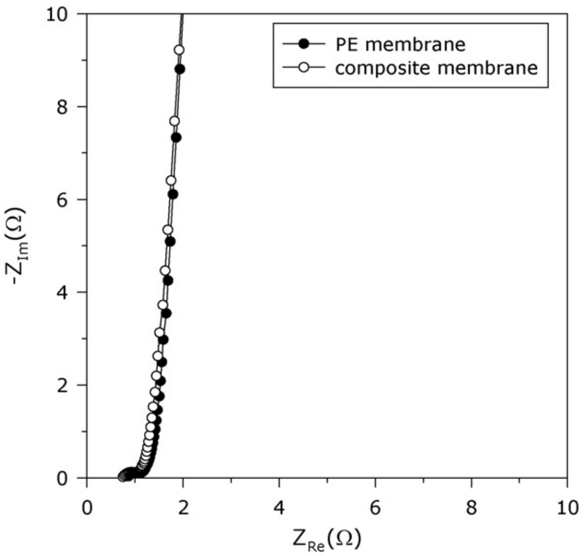
Fig. 3. Discharge capacities of the lithium-ion cells assembled with PE and hybrid composite membranes (0.5 C CC and CV charge, 0.5 C CC discharge, cut-off: 3.0–4.2 V).

of electrolyte absorbed in the porous composite membrane was greater than that absorbed by the PE membrane, which resulted in a higher ionic conductivity. P(VdF-*co*-CTFE) is a copolymer that is easily wetted and swollen by an electrolyte solution. Thus, it had a higher uptake of the electrolyte solution than the hydrophobic PE membrane. In order to compare the heat-resistant properties of the composite membrane to those of the PE membrane, we measured their thermal shrinkages after storage at 105 °C for 1 h. These results are also given in Table 1. It was found that the thermal shrinkage of the hybrid composite membrane was lower than that of the PE membrane. It is considered that the microfibrous web consisting of heat-resistant Al_2O_3 powder and thermally stable P(VdF-*co*-CTFE) polymer on both sides of the porous PE membrane can prevent the dimensional change by thermal deformation because of the frame structure of the ceramic powder with the polymer.

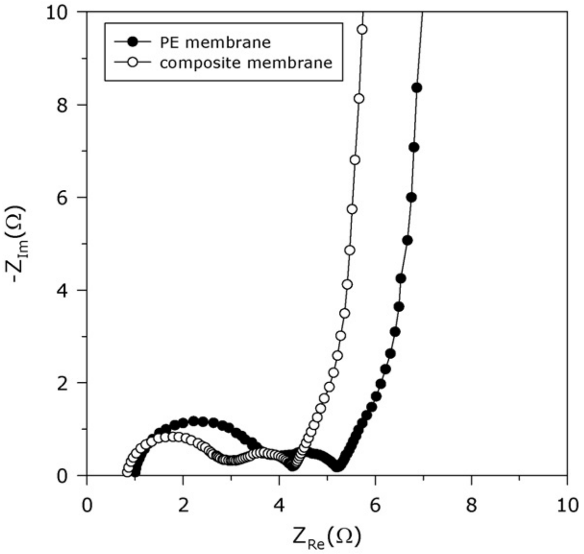
Cycling performance of the lithium-ion cell prepared with the composite membrane was evaluated. The assembled cells were initially subjected to a preconditioning cycle in the voltage range of 3.0–4.2 V at constant current rates of 0.05 C, 0.1 C, and 0.2 C, consecutively. After the three cycles, the cells were charged at a 0.5*C* rate up to a target voltage of 4.2 V. This was followed by a constant voltage charge with declining current until the final current reached 20% of the charging current. Then, it was discharged down to a cut-off voltage of 3.0 V at the same current density (0.5*C* rate). Fig. 2 shows the charge–discharge curves of the 1st, 50th, 100th, and 200th cycle of the lithium-ion cell assembled with the hybrid composite membrane. The cell has an initial discharge capacity of 143.5 mAh g^{-1} based on the $LiCoO_2$ active material in the cathode. The discharge capacity of the cell declines to 131.8 mAh g^{-1} at the 200th cycle, which corresponds to 88.1% of the initial discharge capacity. The coulombic efficiency steadily increased and stabilized with cycle number and was 99.6% at the 200th cycle.

Fig. 3 shows the discharge capacities of the lithium-ion cells fabricated with a PE membrane and a composite membrane as a function of the number of cycles. The initial discharge capacities are found to be little dependent on the membrane type. On the other hand, the cell assembled with a composite membrane exhibited better capacity retention than that of the cell assembled with a PE membrane. The electrospun fibers coated on the PE membrane swell when soaked in liquid electrolyte and take a hold of the electrolyte solution preventing its leakage during repeated cycling. The swollen phase also helps to adhere the membrane to the electrodes through cycling. As a result, the cell assembled with the composite membrane demonstrated improved capacity retention behavior.

In order to investigate the effect of the type of separator on the impedance behavior of the cell, the AC impedance of the cells before and after the repeated cycles (200 cycles) was measured in the discharged state. It has been known that AC impedance spectrum of lithium-ion cell depends on the state of charge [23]. For a fair comparison, we tried to investigate the AC impedance behavior in the discharged state. The resultant AC impedance spectra are shown in Fig. 4. Fig. 4(a) was obtained at the open circuit potential before cycling and Fig. 4(b) was measured at discharged state after 200 cycling. At the open circuit potential before cycling, the two cells exhibited almost identical AC impedance spectra except for a small difference in the electrolyte resistance. This result indicates that the coating of microfibers consisting of P(VdF-*co*-CTFE) and Al_2O_3 powder on the PE membrane has little effect on the interfacial resistance in the cell before cycling. In the cells, the amount of electrolyte absorbed in the porous hybrid composite membrane was greater than that absorbed by the PE membrane, which resulted in a lower electrolyte resistance for composite membrane. After charge and discharge cycling, two semicircles are found, as observed in Fig. 4(b). According to previous AC impedance analysis studies [24,25], the semicircle in the high frequency range can be attributed to the resistance due to Li^+ ion migration through the surface film on the electrode and the semicircle in the medium to low frequency range is due to charge transfer resistance between the electrode and electrolyte. It was found that the charge transfer resistance observed in the medium to low frequency region is only slightly affected by the type of membrane. On the other hand, the surface film resistance was found to be lower in the cell assembled with the composite membrane. It is well known that the addition of nano-sized ceramic filler is a useful tool for enhancing the electrical and mechanical properties of polymer electrolytes [15–17,26,27]. In a composite membrane, the electrospun fiber consisting of Al_2O_3 powder with a high surface area and hydrophilic P(VdF-*co*-CTFE) can hold the solvent effectively and the reactivity between the organic solvent and the electrodes is decreased, which can limit the growth of the resistive layer on the electrodes. This result is consistent with the results of previous work that showed that the addition of nano-sized Al_2O_3 filler improved the interfacial stability between the electrode and the electrolyte [27]. It should also be noted that the electrolyte resistance estimated from the intercept on the real axis increased to 119% of the initial resistance after 200 cycles in the cell prepared with the PE membrane, while the value increased to 109% for the cell with the composite membrane. This result means that the electrolyte solution is well



(a) before cycling



(b) after 200 cycles

Fig. 4. AC impedance spectra (a) before and (b) after cycling of the lithium-ion cells assembled with different membranes.

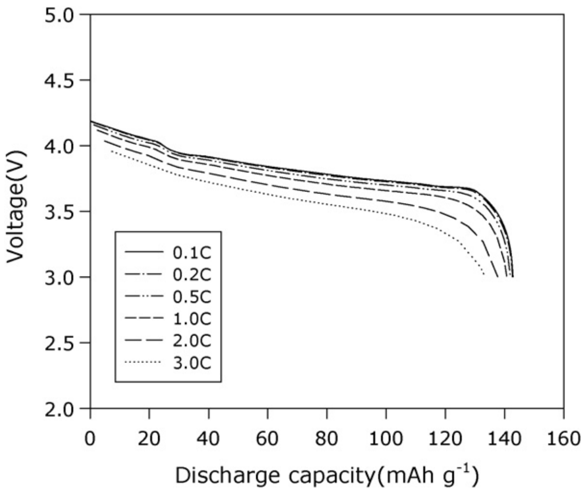


Fig. 5. Discharge profiles of the lithium-ion cell prepared with the hybrid composite membrane as a function of the *C* rate. The charge rate was 0.2 C with a 4.2 V cut-off.

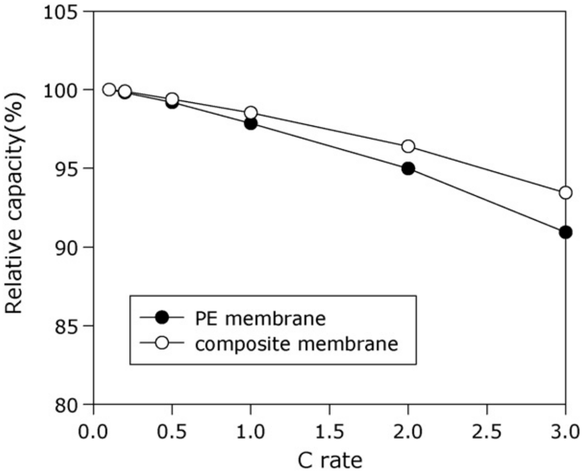


Fig. 6. Relative capacities of the lithium-ion cells prepared with PE and hybrid composite membranes as a function of the *C* rate.

encapsulated during cycling in the cell prepared with the composite membrane.

The rate capability of the lithium-ion cell prepared with the composite membrane was evaluated. The cell was charged to 4.2 V at a constant current rate of 0.2 C and discharged at different current rates from 0.1 C to 3.0 C. The discharge curves of the lithium-ion cell assembled with the composite membrane at different *C* rates are given in Fig. 5. The cell delivered a high discharge capacity (133 mAh g^{-1}) even at a 3.0*C* rate, where its discharge capacity was 93% compared to that obtained at a 0.1*C* rate. This high rate performance of the cell may be partially ascribed to the low loading level of active materials in the electrode. Fig. 6 compares the relative discharge capacities of lithium-ion cells prepared with the PE and composite membranes as a function of current density. The relative capacity is defined as the ratio of the discharge capacity at a specific *C* rate to the discharge delivered at a 0.1*C* rate. It is clear that the presence of electrospun fibers on the PE leads to a higher capacity at a high current rate. The improved rate performance of the cell prepared with a composite membrane is related to the low electrolyte resistance and reduced formation of a resistive surface film on the electrode, as illustrated in Fig. 4.

4. Conclusions

P(VdF-*co*-CTFE) and Al_2O_3 powder in microfibrous form were coated on both sides of a PE membrane by an electrospinning method. The composite membrane showed better thermal stability and wettability for liquid electrolyte solution than PE membrane. A lithium-ion cell assembled with the composite membrane exhibited good capacity retention and high rate performance due to the effective encapsulation of the electrolyte solution in the cell and the adhesive properties of the swollen polymer electrolyte towards electrodes. A hybrid composite membrane prepared by the electrospinning method can be a good microporous separator with enhanced thermal stability and good cycling performance for application in lithium-ion batteries.

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