Evaporation-induced, close-packed silica nanoparticle-embedded nonwoven composite separator membranes for high-voltage/high-rate lithium-ion batteries: Advantageous effect of highly percolated, electrolyte-philic microporous architecture

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1. Introduction

A rapid expansion of lithium-ion batteries into newly emerging application fields such as smart mobile devices, (hybrid) electric vehicles, and energy storage systems triggers strong demand for the urgent development of high-energy density/high-power density cells, however, which entails confronting formidable challenges related to safety failures [1–4]. The aforementioned electrochemical performance and safety concerns are strongly influenced by core components (i.e., anode, cathode, electrolyte, and separator) of cells. In particular, when internal short-circuit of cells, the most critical threat in securing battery safety, is issued, a separator is considered a key component to prevent the problem, because its primary role is to maintain electrical isolation between the cathode and anode [5–8]. Another important function of a separator is to allow ionic transport via its micropores filled with liquid electrolytes. Ionic conductivity of a separator is known to critically affect ohmic polarization (i.e., IR drop) of a cell, which may become more significant at harsh charge/discharge conditions such as high voltages and high current densities.

Currently, most widely used separators in lithium-ion batteries are manufactured from polyolefins, predominantly polyethylene (PE) or polypropylene (PP) [7,8]. These polyolefin separators have many advantages in terms of practical application to commercialized lithium-ion batteries, however, due to poor thermal shrinkage and weak mechanical strength of the polyolefin separators, it is difficult to fully ensure electrical isolation between electrodes. Moreover, their intrinsically hydrophobic character and low porosity have often raised serious concerns over insufficient electrolyte wettability, which could directly impair the ion transport through polyolefin separators. Hence, an advanced separator that can overcome these stringent shortcomings of the polyolefin separators is imperiously needed for facilitating the successful development of high-energy density/high-power density cells.

Among various approaches used to achieve this goal, the incorporation of nonwovens that consist of multi-fibrous layers has drawn considerable attention due to their excellent thermal properties, high porosity, and cost competitiveness [9–16]. In our
In previous studies [14,15], we introduced new nonwoven-based composite separators that were composed of microporous polyvinylidene fluoride–hexafluoropropylene (PVdF–HFP) gel polymer electrolytes and polyethylene terephthalate (PET) nonwoven supports. The microporous structure of the composite separators was determined by controlling the phase inversion of coating solutions (PVdF–HFP/acetone (solvent)/water (nonsolvent)). The effects of phase inversion-governed, microporous morphology on the thermal stability and electrochemical performance of the composite separators were also investigated.

In the present study, in a continued effort to develop promising nonwoven-based separators, we demonstrate a facile approach to fabricate a silica (SiO₂) nanoparticle/PVdF–HFP-coated PET nonwoven composite separator (hereinafter, referred to as “NW-separator”) by exploiting a concept of evaporation-induced, close-packed nanoparticle arrays [16–19], where the heat-resistant PET nonwoven is employed as a physical support to prevent thermal shrinkage of the NW-separator. In contrast to conventional nanocomposites, where nanoparticles are dispersed in polymer matrices, the NW-separator proposed in this study is featured with well-connected interstitial voids formed between compactly packed SiO₂ nanoparticles, wherein the PVdF–HFP acts as a binder to adhere SiO₂ nanoparticles rather than existing as a continuous phase. This anomalous nanoparticle arrangement is expected to allow for the evolution of highly percolated, electrolyte-philic microporous architecture in the NW-separator.

Another important objective of the present study is to explore the feasibility of applying the NW-separator to high-voltage/high-rate lithium-ion batteries that have recently garnered increasing attention. Membrane characteristics of the NW-separator are evaluated in terms of porous structure, thermal shrinkage, electrolyte wettability, and ionic conductivity. Based on this solid understanding of separator properties, the effect of the NW-separator on cell performance, particularly at challenging charge/discharge conditions of high voltages (herein, 4.4 V) and high current densities, is investigated and the results are compared with those obtained with a commercialized PE separator.

2. Experimental

2.1. Fabrication of SiO₂/PVdF–HFP-coated nonwoven composite separator (NW-separator)

The coating solution was prepared by mixing SiO₂ nanoparticles (average particle size = 40 nm) and PVdF–HFP (HFP content = 6 mol%) in acetone, where the SiO₂/PVdF–HFP composition ratio was fixed at 90/10 (wt%/wt%). In comparison to the SiO₂ nanoparticles, the PVdF–HFP binder itself is expected to have insignificant influence on the properties of NW-separator because of its very small content. After dissolving PVdF–HFP in acetone, a predetermined amount of SiO₂ powders was added and then the solution was further subjected to intensive mixing via bead-milling for 1 h. A wet-laid PET nonwoven (thickness = 17 μm) was soaked in the aforementioned coating solution for 3 min using a dip-coating process. The evaporation-induced, close-packing of SiO₂ nanoparticles was realized between the PET fibers by slowly drying the coating solution-immersed PET nonwoven at room temperature, followed by vacuum drying at 50 °C for 4 h. The final thickness of NW-separator was observed to be approximately 30 μm. Meanwhile, as a control sample, a commercialized PE separator (thickness ~ 20 μm, Tonen) was chosen.

2.2. Characterization of membrane properties and cell performance of NW-separator

The surface and cross-sectional porous structure of NW-separator was examined using field emission scanning electron microscopy (FE-SEM, S-4300, Hitachi). The porosity of NW-separator, \( \phi_p(\%) \), was estimated using the following equation [20–22]:

\[
\phi_p(\%) = 1 - \left[ \frac{W_C}{\rho_C + W_N/\rho_N} \right] / V_{NS} \times 100
\]

where \( W_C \) is the weight per square meter of the SiO₂/PVdF–HFP coating layer (= 11.3 g), \( W_N \) is the weight per square meter of the PET nonwoven (= 10.0 g), \( \rho_C \) is the density of the SiO₂/PVdF–HFP coating layer (= 2.5 g cm\(^{-3}\)), \( \rho_N \) is the density of the PET nonwoven (= 1.4 g cm\(^{-3}\)), and \( V_{NS} \) is the volume of the NW-separator.
The air permeability of separators was evaluated with a Gurley densometer (4110N, Gurley) by measuring the time necessary for air to pass through a determined volume under a given pressure, where a low Gurley value (≤100 cm$^{-3}$) represents high air permeability. The thermal shrinkage of separators was determined by measuring their (area-based) dimensional change after exposure to various temperatures for 0.5 h. For characterization of electrochemical performance of separators, a liquid electrolyte of 1 M LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1 v/v) was employed. The electrolyte wettablity of separators was examined measuring their (area-based) dimensional change after exposure to various temperatures for 0.5 h. For characterization of electrochemical performance of separators, a liquid electrolyte of 1 M LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1 v/v) was employed. The electrolyte wettablity of separators was examined

\[
\text{Table 1}
\]

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Porosity (%)</th>
<th>Gurley value (≤100 cm$^{-3}$)</th>
<th>Ionic conductivity (mS cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE separator</td>
<td>~20</td>
<td>45</td>
<td>240</td>
</tr>
<tr>
<td>NW-separator</td>
<td>~30</td>
<td>61</td>
<td>41</td>
</tr>
</tbody>
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Fig. 2. A schematic representation illustrating microporous structure and conceptual ion transport of NW-separator.

Fig. 3. (a) Thermal shrinkage of PE separator and NW-separator as a function of heat-treatment temperature. (b) Photographs of the separators after exposure to 150 °C for 0.5 h.

Fig. 4. (a) Photographs exhibiting liquid electrolyte (1 M LiPF$_6$ in EC/DEC = 1/1 v/v) wetting behavior of PE separator and NW-separator. (b) Electrolyte immersion-height of PE separator and NW-separator.

Fig. 5. (a) OCV profiles of cells assembled with NW-separator or PE separator, where the cells are charged to 4.2 V at a constant charge current density of 0.5 C and their voltage drop is measured as a function of elapsed time. (b) Pore size distribution of PE separator, NW-separator, and pristine PET nonwoven.
by observing turbidity change of separator surface after dropping the liquid electrolyte onto the separator and also was quantitatively estimated by measuring the electrolyte immersion-height of the separator. The ion conductivity of separators was obtained by an AC impedance analysis (Bio-Logic) over a frequency range of $10^{-2}$–$10^6$ Hz. A unit cell (2032-type coin) was assembled by sandwiching a separator between a natural graphite anode and a LiCoO$_2$ cathode and then activated by filling the liquid electrolyte. All assembly of cells was carried out in an argon-filled glove box. The discharge capacity, discharge C-rate capability, and cycling performance of cells were investigated using a cycle tester (PNE Solution). The discharge current ranges of 3.0–4.2 and 3.0–4.4 V. For measurement of cycling performance, the cells were cycled at different charge/discharge current densities of 0.2 C and 1.0 C, respectively.

### 3. Results and discussion

Morphological uniqueness of the NW-separator, as compared to a commercialized PE separator and a pristine PET nonwoven, was investigated in terms of porous structure. Fig. 1(a) shows that the PE separator has a large number of micropores with diameter below 0.5 μm. Meanwhile, the pristine PET nonwoven contains excessively large-sized pores (approximately, larger than 5 μm) that are arbitrarily distributed between the PET fibers (Fig. 1(b)). By contrast, considerably different porous structure was observed in the NW-separator. Fig. 1(c) exhibits that the SiO$_2$ nanoparticles adhered by PVdF–HFP binders are closely packed, which allows for the evolution of an unusual porous structure (i.e., well-connected interstitial voids established between the SiO$_2$ nanoparticles) in the NW-separator. Intriguingly, the pore size (i.e., dimension of interstitial voids) of the NW-separator appears to be insignificantly different from that of the PE separator. The porous structure of the NW-separator was further characterized by observing the cross-sectional morphology. Fig. 1(d) confirms that, consistent with the surface morphology, the SiO$_2$ nanoparticles are tightly packed between the PET nonwoven fibers, leading to the construction of highly percolated interstitial voids in the thickness direction of the NW-separator.

This unusual microporous structure (i.e., highly percolated interstitial voids) is a distinctive feature of the NW-separator, in contrast to dense structure of conventional nanocomposite-based separators. The micropores of the NW-separator will be filled with liquid electrolyte and then serve as effective ion-conducting channels during charge/discharge reaction of cells. A schematic representation illustrating the microporous structure and conceptual ion transport of the NW-separator is provided in Fig. 2.

The porous structure of the NW-separator is quantitatively characterized by measuring the Gurley value (i.e., air permeability) and porosity. Table 1 shows that, in comparison to the PE separator (~$240 \times 100$ cm$^{-2}$), the NW-separator presents a lower Gurley value indicating high air permeability (~$41 \times 100$ cm$^{-2}$). This verifies that the highly percolated interstitial voids formed between the close-packed SiO$_2$ nanoparticles can offer a short tortuous path for air transport in the NW-separator. Meanwhile, the Gurley value of the pristine PET nonwoven was too low to be determined (i.e., it was beyond the measuring limit of the instrument), because of its excessively large-sized pores. The highly porous structure of the NW-separator is further confirmed by comparing its porosity (~61%) with that (~45%) of the PE separator. This highly developed porous structure (i.e., low Gurley value and high porosity) of the NW-separator is expected to be beneficial in facilitating ionic transport.

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**Fig. 6.** Discharge profiles of cells (under a voltage range of 3.0–4.2 V at a constant charge current density of 0.2 C) assembled with: (a) NW-separator; (b) PE separator. Comparison of discharge C-rate capability between PE separator and NW-separator under a voltage range of (c) 3.0–4.2 V; (d) 3.0–4.4 V.
Table 1 also exhibits that the NW-separator presents the higher ionic conductivity ($\sim 0.91 \text{ mS cm}^{-1}$) than the PE separator ($\sim 0.73 \text{ mS cm}^{-1}$).

Following this structural characterization of the NW-separator, other important separator properties such as thermal shrinkage, electrolyte wettability, and open circuit voltage (OCV) drop were examined. Fig. 3(a) compares the thermal shrinkage of NW-separator with that of the PE separator by measuring the (area-based) dimensional change, where the separators were subjected to heat treatment at various temperatures for 0.5 h. The NW-separator is difficult to be thermally deformed over a wide range of temperature, whereas the PE separator continues to shrink with an increase of temperature. The difference in the thermal shrinkage between the two separators becomes more noticeable as the temperature is increased from 110 to 150 °C. Fig. 3(b) depicts photographs of the separators after exposure to 150 °C for 0.5 h. This confirms the superior thermal stability of the NW-separator, as compared to the PE separator showing the thermal shrinkage of $\sim 94\%$. The substantially improved thermal shrinkage of the NW-separator is attributed to the incorporation of the PET nonwoven support [13–16]. The PET nonwoven support in the NW-separator is thermally stable, because it has a high melting temperature above 250 °C and does not experience stretching processes that are essentially employed for manufacturing a PE separator [6–8].

The intrinsically hydrophobic characteristic of PE separators often provokes grave concerns about electrolyte wettability [5–9]. In particular, in large-sized batteries, which attract considerable attention in various application fields such as (hybrid) electric vehicles and energy storage systems, fast and uniform wetting of the liquid electrolyte over the entire separator poses a formidable challenge. Fig. 4(a) shows that, in comparison to the PE separator, the NW-separator is quickly wetted with the liquid electrolyte (herein, 1 M LiPF$_6$ in EC/DEC=1/1 v/v), where the electrolyte droplets easily spread over a wide area of the NW-separator. The improved wettability of the NW-separator is further confirmed by quantitatively measuring the electrolyte immersion-height (Fig. 4(b)). After an elapsed time of 60 min, the NW-separator shows the higher electrolyte immersion-height (\sim 1.6 cm) than the PE separator (\sim 0.5 cm). This electrolyte-philic character of the NW-separator is attributed to the relatively high polarity of their components (i.e., SiO$_2$, PVdF-HFP, and PET) and the highly percolated interstitial voids, both of which could be advantageous in facilitating the capillary intrusion [14–16] of liquid electrolyte into the micropores of NW-separator.

An OCV drop of cells is considered to deliver useful information on self-discharge, which in turn can predict the risk of internal short-circuits between electrodes. The OCV behavior of cells is known to be significantly influenced by porous structure of separators [6–9,14–16]. A separator with excessively large-sized pores and nonuniform pore size distribution tends to inadequately suppress leakage current between electrodes, resulting in a decrease of the OCV. Herein, the cells were charged to 4.2 V and their voltage drop was measured as a function of elapsed time. Fig. 5(a) shows that there is little difference in the OCV profiles between the PE separator and NW-separator. By contrast, the cell assembled with the pristine PET nonwoven presents a dramatic decline of the OCV in a very short time. This strong dependence of OCV behavior on separator types can be further explained by scrutinizing the pore size and pore size distribution of the separators. Fig. 5(b) exhibits that, in good agreement with the morphological results (Fig. 1), the NW-separator has small-sized pores and also narrow pore size distribution, where most pores are below 0.5 $\mu$m in size. On the other hand, the pristine PET nonwoven shows immoderately large pore size (\> 5.0 $\mu$m) and a broad pore size distribution, and thus may fail to prevent leakage current between electrodes [10,14,16]. These OCV results demonstrate that the NW-separator has the well-tuned pore size and pore size distribution that can effectively prevent the self-discharge of cells.

The discharge capacities of cells assembled with the NW-separator were evaluated as a function of discharge current density, where the cells were charged under a voltage range of 3.0–4.2 V at a constant charge current density...
of 0.2 C and discharged at various current densities ranging from 0.2 to 2.0 C. Fig. 6(a) shows that the voltage and discharge capacity of cells incorporating the NW-separator gradually decrease with an increase of discharge current density, which is similar to the discharge profiles of cells assembled with the PE separator (Fig. 6(b)). An intriguing finding is that the NW-separator exhibits higher discharge capacities than the PE separator over a wide range of discharge current densities. This difference in the discharge capacities between the separators becomes larger at higher discharge current densities, where the influence of ionic transport on ohmic polarization [6–8,24,25] is more significant. Fig. 6(c) summarizes the aforementioned discharge capacities of the NW-separator and PE separator as a function of the discharge current density (i.e., discharge C-rate).

The superior discharge C-rate capability of the NW-separator can be explained by considering its ionic conductivity. It was already shown in Fig. 1 and Table 1 that the highly porous morphology and good electrolyte wettability are obtained in the NW-separator, leading to the provision of higher ionic conductivity. As a result, the facile ion transport of the NW-separator could contribute to the better discharge C-rate capability of cells [14–16]. Moreover, even under a higher charge voltage of 4.4 V (Fig. 6(d)), the NW-separator exhibits higher discharge C-rate capability than the PE separator. These results of the discharge C-rate capability verify the potential application of the NW-separator to high-voltage/high-rate lithium-ion batteries.

The cycling performance (i.e., discharge capacities of cells as a function of cycle number) of the NW-separator was compared with that of the PE separator (Fig. 7). The cells were cycled up to 100 cycles at different charge/discharge current densities of 0.5/0.5 C and 1.0/1.0 C. A charge/discharge condition of 0.5/0.5 C under a range of 2.0–4.2 V, the NW-separator shows higher discharge capacity up to the 100th cycle, as compared to the PE separator (Fig. 7(a)). The gap in the discharge capacity between both the separators becomes larger at a higher charge/discharge current density of 1.0/1.0 C, which boosts the influence of IR drop (Fig. 7(b)). Moreover, even at a higher charge voltage (4.4 V) condition, the NW-separator also provides better cyclability than the PE separator (Fig. 7(c)). The notable improvement in the cycling performance of the NW-separator may be due to its highly percolated microporous architecture and also strong affinity for liquid electrolyte, as these factors could impart more facile ion transport and better electrolyte retention during cycling.

The superior cycling performance of the NW-separator can be further confirmed by analyzing the AC impedance spectra of cells after the 10th and 100th cycle (herein, at a voltage range of 3.0–4.2 V and charge/discharge current density of 0.5/0.5 C). An increase in cell impedance during cycling is known to have a detrimental influence on cell capacity retention of cells [25–30]. Fig. 7(d) shows that the AC impedance of a cell assembled with the PE separator significantly increases after the 100th cycle ($Z_{100}$). By comparison, the NW-separator strongly mitigates the increase in the cell impedance ($Z_{100}$). This suppressed growth of cell impedance, which reflects stabilized interface between the NW-separator and electrodes, may be due to the beneficial contact of the electrolyte-filled NW-separator (more specifically, the SiO$_2$ coating layer having highly percolated, electrolyte-phobic interstitial voids) with the electrodes during cycling. Previous studies [25,29,30] reported that the introduction of ceramic coating layers to separators was effective in suppressing the growth of cell impedance, which thus contributed to the better cycling performance.

The aforementioned results of the cell performance (i.e., discharge capacities, discharge C-rate capability, and cyclability) demonstrate that the NW-separator can be recommended as a promising alternative to a commercialized PE separator for application in next-generation lithium-ion batteries demanding high voltages and high current densities.

### 4. Conclusions

We have developed the evaporation-induced, close-packed SiO$_2$ nanoparticle-embedded PET nonwoven composite separators (“NW-separator”) for lithium-ion batteries. The incorporation of a heat-resistant PET nonwoven support enabled the drastic improvement in the thermal shrinkage of the NW-separator. A salient feature of the NW-separator was the well-connected interstitial voids established between the densely packed SiO$_2$ nanoparticles. This allowed the evolution of highly percolated, electrolyte-phobic microporous architecture in the NW-separator. The porous structure (more specifically, pore size and pore size distribution) of the NW-separator was sufficiently tuned to prevent the self-discharge of cells. In comparison to the PE separator, the NW-separator exhibited lower Gurley value, higher porosity, better electrolyte wettability, and benign contact with electrodes, which contributed to the facile ion transport and mitigated growth of cell impedance during cycling. As a consequence, significantly improved cell performance was obtained in the NW-separator. Notably, this beneficial effect of the NW-separator on cell performance became more pronounced at harsh charge/discharge conditions of high voltages (herein, 4.4 V) and high current densities. In conclusion, the NW-separator proposed in this study can be recommended as a promising alternative to outperform a commercialized PE separator, particularly for use in high-voltage/high-rate lithium-ion batteries that concomitantly demand high-safety.

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