



Short communication

Close-packed SiO₂/poly(methyl methacrylate) binary nanoparticles-coated polyethylene separators for lithium-ion batteriesJang-Hoon Park^a, Joo-Hyun Cho^a, Woong Park^a, Dongjo Ryoo^b, Su-Jin Yoon^c, Jong Hun Kim^c, Yeon Uk Jeong^d, Sang-Young Lee^{a,*}^a Department of Chemical Engineering, College of Engineering, Kangwon National University, Chuncheon, Kangwondo 200-701, Republic of Korea^b Petrochemical R&D, LG Chem, Yusong-gu, Daejeon 305-380, Republic of Korea^c Batteries R&D, LG Chem, Yusong-gu, Daejeon 305-380, Republic of Korea^d School of Materials Science and Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea

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ABSTRACT

In an endeavour to improve not only the thermal shrinkage but also the electrochemical performance of separators in lithium-ion batteries, a novel composite separator is developed, i.e., a close-packed SiO₂/poly(methyl methacrylate) (PMMA) binary nanoparticles-coated polyethylene (PE) separator. The introduction of SiO₂ nanoparticles to the coating layer effectively suppresses thermal shrinkage of the composite separator. In contrast to a SiO₂/PMMA coating layer having a film-shaped PMMA binder, the SiO₂/PMMA binary nanoparticle coating layer employs PMMA particles as a binder. As a consequence, a highly porous structure, i.e., well-connected interstitial voids, is formed between the binary SiO₂ and PMMA nanoparticles. The unique porous morphology allows favourable liquid electrolyte wettability and facile ionic conduction, which play a crucial role in improving cell performance such as the discharge capacity and the C-rate capability of the composite separator.

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1. Introduction

From the viewpoint of lithium-ion battery safety, the separator is considered to be a key component to suppress undesirable collapses, as its primary function is to maintain physical isolation between the cathode and the anode [1,2]. Polyolefin-based separators are widely used and offer many advantages. Nevertheless, their poor thermal stability and low mechanical strength have raised serious concerns over their ability to maintain the necessary electrical isolation between electrodes, particularly under harsh conditions such as abnormal heating or mechanical rupture. Among the variety of approaches to overcome these drawbacks, the introduction of ceramic composite layers has attracted substantial attention, due to their superiority in preventing thermal shrinkage and mechanical breakdown of the separators [3–5]. These layers generally consist of inorganic oxide-based powders and gel polymer electrolytes functioning as binders.

In addition to the safety-reinforcing properties, a major objective for advanced separators is to improve their electrochemical

performances. Meanwhile, gel polymer electrolytes are known to exhibit lower ionic conductivity than liquid electrolytes [6–9]. This implies that the use of gel polymer electrolytes as a binder in ceramic composite layer-based separators may deteriorate the ionic conduction, which becomes more serious when operating at high charge/discharge currents. In this study, in order to overcome these limitations of ceramic composite layers and gear up their application to separators particularly in high-power lithium-ion batteries, a novel approach is demonstrated and is based on introducing close-packed inorganic oxide/polymer binary nanoparticles as a ceramic composite layer.

Well-controlled nanoparticle arrangement driven by self-assembly has attracted much attention as an ideal starting template [10–12] for the preparation of porous materials that could be used in various applications that range from sensors to catalysts. Exploiting the concept of these unique colloidal templates, close-packed SiO₂/PMMA binary nanoparticle (hereinafter, referred to as SiO₂/PMMA-BNP) coating layers are applied to both sides of a PE separator. A key feature of this ceramic composite layer is that PMMA particles are employed as the binder, instead of a conventional, film-shaped PMMA binder. SiO₂ and PMMA are selected as a representative inorganic oxide and binder, respectively. A major objective of the study is to investigate the effects of the SiO₂/PMMA-BNP coating layers on liquid electrolyte wettability

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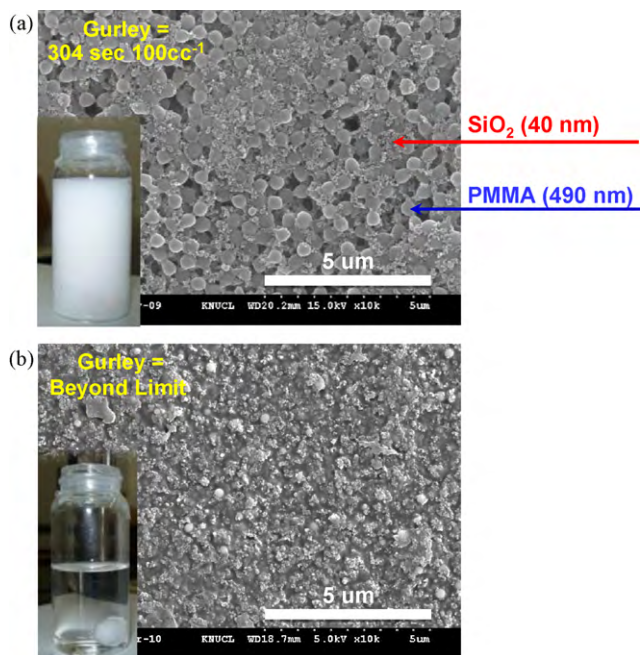


Fig. 1. FE-SEM photographs (surface) of (a) SiO₂ (average particle size = 40 nm)/PMMA (average particle size = 490 nm)-BNP coating layer and (b) SiO₂/PMMA coating layer. Insets represent PMMA colloidal solution and PMMA/acetone solution, respectively.

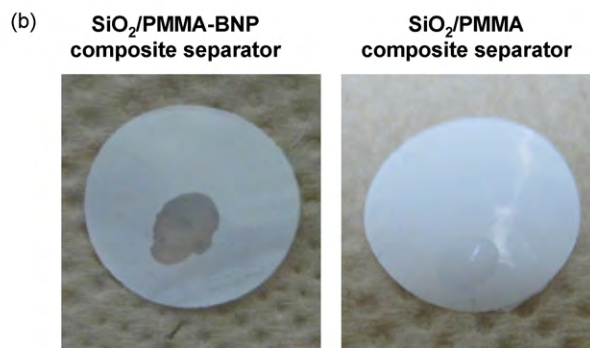
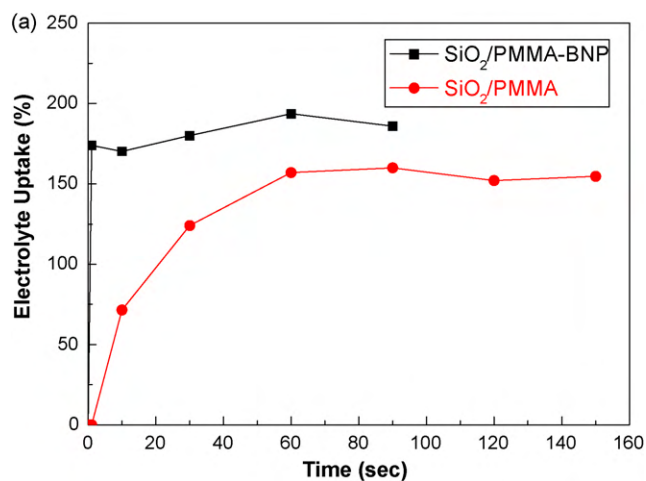


Fig. 2. (a) Liquid electrolyte uptake of SiO₂/PMMA-BNP composite separator and SiO₂/PMMA composite separator as function of wetting time. (b) Photographs showing liquid electrolyte wetting behaviour of different separators.

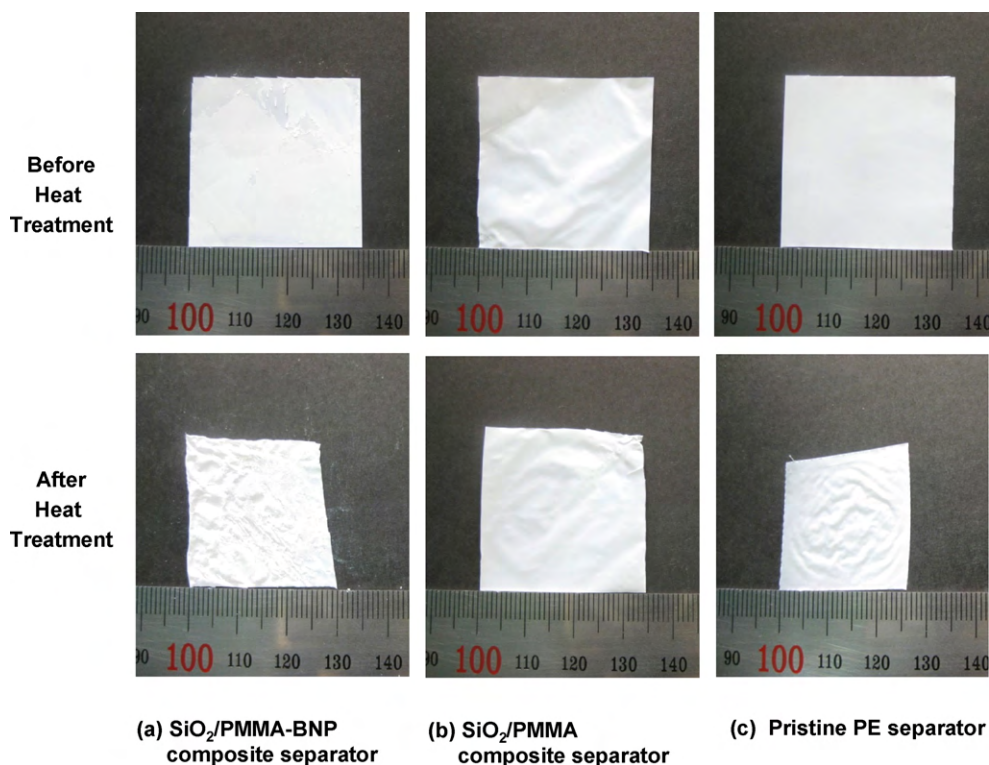


Fig. 3. Thermal shrinkage of (a) SiO₂/PMMA-BNP composite separator; (b) SiO₂/PMMA composite separator; and (c) pristine PE separator, where separators are subjected to heat treatment at 120 °C for 0.5 h.

ity, thermal shrinkage, ionic conductivity and, more importantly, cell performance such as discharge capacity and C-rate capability. A comparison is made with results obtained from conventional SiO₂/PMMA coating layers.

2. Experimental

A PMMA particle (average particle size = 490 nm) colloidal solution (inset in Fig. 1a) was prepared by conventional emulsion polymerization. The detailed synthesis procedure has been described in previous publications [13,14]. Unlike the transparent PMMA solution (inset in Fig. 1b), the PMMA colloidal solution was white in colour due to light scattering by the PMMA particles dispersed in the water. The SiO₂ powder-dispersed solution was prepared by adding a fixed amount of SiO₂ powder (average particle size = 40 nm) to distilled water and the solution was then subjected to ball-milling for 2 h. The SiO₂ powder-dispersed solution was mixed with the PMMA colloidal solution via mechanical stirring, where a composition ratio of SiO₂:PMMA was fixed at 50:50 (wt.:%:wt.:%). As a control sample, a transparent PMMA solution was prepared by dissolving PMMA powder in acetone. The PMMA powder was obtained by evaporating water from the PMMA colloidal solution. The PMMA solution was mixed with SiO₂ powder (SiO₂:PMMA = 50:50, wt.:%:wt.:%) and the solution was further subjected to ball-milling for 2 h. As a coating substrate, a PE separator (thickness = 20 μm, Gurley value = 240 s 100 cc⁻¹, ExxonMobil) was chosen. The SiO₂/PMMA colloidal solution or the conventional SiO₂/PMMA solution was applied to both sides of the PE separator by a dip-coating process. The separator was then dried at room temperature to evaporate the solvent and was further vacuum dried at 50 °C for 12 h. The final thickness of the separator was observed to be around 28 μm.

The air permeability of the separators was examined using a Gurley densometer (Gurley). The morphologies of the coating layers were investigated by a field emission scanning electron microscope (Hitachi) in the central laboratory of Kangwon National University. The thermal shrinkage of the separators was determined by measuring their dimensional change (area-based) after they were subjected to heat treatment at 120 °C for 0.5 h [5]. The liquid electrolyte wettability (1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) = 1:1, v:v, Techno Semichem) was examined by measuring the electrolyte uptake as a function of wetting time. The ionic conductivity of the separators was measured by carrying out a.c. impedance analysis (Bio-Logic) over a frequency range of 0.1 to 10⁶ Hz. Lithium half-cells (2032-type coin) were assembled by sandwiching the separator between a lithium-metal anode and a LiCoO₂ cathode, and then were activated by introducing the liquid electrolyte. The discharge capacities of the cells were examined as a function of discharge current density using a cycle tester (PNE Solution). Discharge current densities between 0.2 C (=0.68 mA cm⁻²) and 2.0 C (=6.80 mA cm⁻²) were employed at a constant charge current density of 0.2 C under a voltage range of 3.0–4.3 V.

3. Results and discussion

The FE-SEM photograph in Fig. 1a shows that a SiO₂/PMMA-BNP coating layer is successfully formed on the PE separator, where the SiO₂ (particle size = 40 nm) and PMMA powders (particle size = 490 nm) are well mixed with each other. It is noteworthy that highly connected interstitial voids are formed between the close-packed binary nanoparticles. These unique interstitial voids are expected to play an important role in improving liquid electrolyte wettability and ionic conduction. By contrast, a porous structure is not observed in the SiO₂/PMMA coating layer (Fig. 1b). Due to

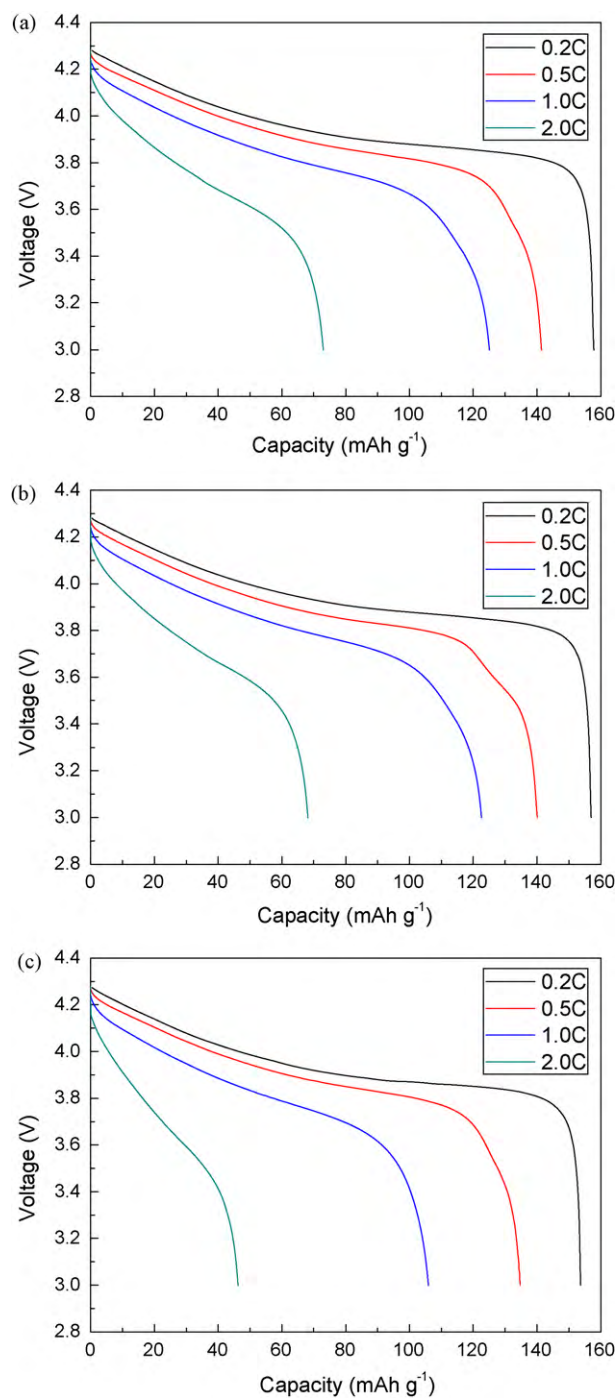


Fig. 4. Discharge profiles of cells assembled with: (a) pristine PE separator; (b) SiO₂/PMMA-BNP composite separator; and (c) SiO₂/PMMA composite separator, where discharge current densities are varied from 0.2 C (=0.68 mA cm⁻²) to 2.0 C (=6.80 mA cm⁻²) at constant charge current density of 0.2 C over voltage range of 3.0–4.3 V.

the existence of film-shaped PMMA binder, the SiO₂/PMMA coating layer presents a dense structure.

The porous structure of SiO₂/PMMA-BNP coating layers was quantitatively characterized by measuring the air permeability of the separators. The air permeability, as represented by the Gurley value (s 100 cc⁻¹), is considered to be a useful property for quantitatively characterizing a porous structure, where a low Gurley value indicates high air permeability. Thus, the Gurley value could be used to predict the ionic conductivity of a separator [1,2].

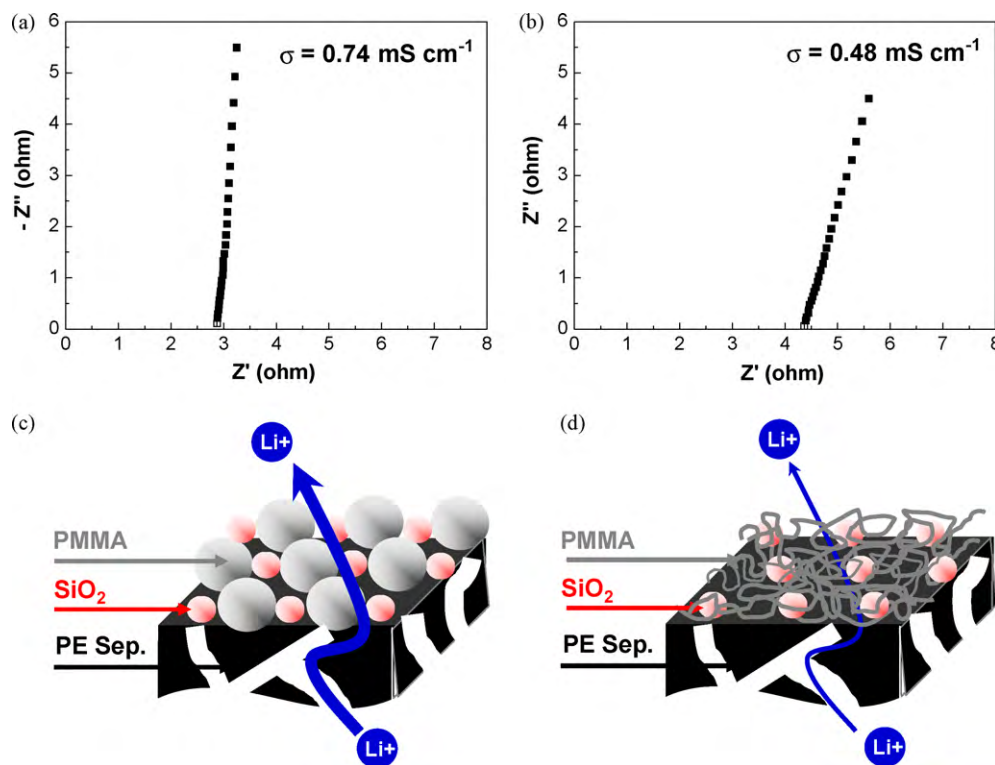


Fig. 5. Ionic conductivity of: (a) $\text{SiO}_2/\text{PMMA-BNP}$ composite separator and (b) SiO_2/PMMA composite separator. Schematic illustrations of the structure and ionic transport of (c) $\text{SiO}_2/\text{PMMA-BNP}$ composite separator and (d) SiO_2/PMMA composite separator (bold arrow signifies more facile ionic transport).

The Gurley value of the $\text{SiO}_2/\text{PMMA-BNP}$ composite separator was observed to be $304 \text{ s } 100 \text{ cc}^{-1}$, whereas that of the conventional SiO_2/PMMA composite separator was too high to be measured, i.e., it was beyond the measurement limit of the instrument. This result on the air permeability, along with morphological observations, indicates that a porous structure is successfully developed in the $\text{SiO}_2/\text{PMMA-BNP}$ coating layer.

The liquid electrolyte uptake of the composite separators was investigated as a function of wetting time. Fig. 2a shows that the $\text{SiO}_2/\text{PMMA-BNP}$ composite separator is quickly wetted by the liquid electrolyte and its electrolyte uptake becomes saturated within a very short wetting time. On the other hand, the SiO_2/PMMA composite separator requires a relatively long wetting time, roughly 60 s is required to reach the saturated level of electrolyte uptake. This improvement in the liquid electrolyte uptake of the $\text{SiO}_2/\text{PMMA-BNP}$ composite separator was further confirmed by observation of the separator surface after dropping liquid electrolyte on the separator. Fig. 2b shows that the $\text{SiO}_2/\text{PMMA-BNP}$ composite separator is highly effective in absorbing liquid electrolyte, compared with the SiO_2/PMMA composite separator. This superior electrolyte uptake may be attributed to the unique porous structure of the $\text{SiO}_2/\text{PMMA-BNP}$ coating layer, where the liquid electrolyte can infiltrate preferentially through the well-connected interstitial voids, possibly driven by capillary force. On the other hand, in the case of the SiO_2/PMMA coating layer, its electrolyte uptake proceeds through the free volume in PMMA [6,7]. Another interesting finding is that the $\text{SiO}_2/\text{PMMA-BNP}$ composite separator shows a larger amount of electrolyte uptake ($\sim 180\%$), compared with the SiO_2/PMMA composite separator ($\sim 150\%$). This difference in electrolyte uptake can also be explained by considering the porous structure of the $\text{SiO}_2/\text{PMMA-BNP}$ coating layer, because a porous structure can absorb larger amounts of liquid than a dense structure [15,16].

As lithium-ion batteries rapidly expand to new applications such as electric vehicles and power tools that generally necessitate

large-sized batteries, fast and uniform electrolyte uptake by separators poses a major challenge. Meanwhile, due to battery safety concerns, the use of ceramic layer-coated separators in large-sized batteries is becoming widespread. Therefore, the unique porous structure of the $\text{SiO}_2/\text{PMMA-BNP}$ coating layer is expected to be a promising approach to improving the wettability of composite separators.

Thermal shrinkage of the composite separators was observed by measuring their (area-based) dimensional change after being subjected to heat treatment at 120°C for 0.5 h. Since conventional PE separators have a melting point of about 135°C and are prepared through multiple stretching processes, they easily lose dimensional stability upon exposure to high temperatures above 100°C . Fig. 3 shows that the thermal shrinkage ($\sim 10\%$) of the $\text{SiO}_2/\text{PMMA-BNP}$ composite separator is slightly larger than that ($\sim 5\%$) of the SiO_2/PMMA composite separator. This may be attributed to the porous structure of the $\text{SiO}_2/\text{PMMA-BNP}$ coating layer. Previous studies [3–5] reported that the thermal stability of composite separators depends highly on the structure of ceramic composite layers, i.e., the relatively dense structure of ceramic composite layers is known to be more effective in preventing the thermal shrinkage of separators. Although the $\text{SiO}_2/\text{PMMA-BNP}$ composite separator seems to be marginally inferior to the SiO_2/PMMA composite separator in terms of thermal stability, it is apparent that it provides improved thermal shrinkage compared with a pristine PE separator ($\sim 30\%$). Comparison of the thermal shrinkage between the separators stresses that the introduction of a $\text{SiO}_2/\text{PMMA-BNP}$ coating layer on the PE separator can be effective in preventing thermal shrinkage of the separator.

The effect of morphological differences between the composite separators on the electrochemical performance of cells has been investigated. The discharge profiles of cells assembled with the composite separators are represented in Fig. 4. The cells were charged over a voltage range of 3.0–4.3 V at a constant current density of 0.2 C and discharged at different current densities rang-

ing from 0.2 to 2.0C. No abnormal or unstable discharge profiles are observed for the composite separators. As the discharge current density increases, the voltage and discharge capacity of the cells tend to gradually decrease. Comparison of the data in Fig. 4a and b demonstrates that the discharge C-rate capacities of the SiO₂/PMMA-BNP composite separator appear to be comparable with those of the pristine PE separator, which reveals that the SiO₂/PMMA-BNP coating layer does not significantly hinder ionic conduction owing to its well-developed porous structure. An interesting finding is that the SiO₂/PMMA-BNP composite separator (Fig. 4b) shows larger discharge capacities than the SiO₂/PMMA composite separator (Fig. 4c). In particular, the difference in the discharge capacity between the two composite separators becomes larger at higher discharge current densities, where the influence of ionic transport on ohmic overpotential (i.e., IR drop) is more significant. In general, gel polymer electrolytes are known to exhibit lower ionic conductivity than liquid electrolytes [6–9]. The SiO₂/PMMA-BNP coating layers have a highly developed porous structure that will be filled with liquid electrolyte, whereas the SiO₂/PMMA coating layer presents a film-shaped PMMA binder that functions as a gel polymer electrolyte. Therefore, the porous structure of the SiO₂/PMMA-BNP coating layers could be beneficial in improving the discharge C-rate capability of cells, in comparison with the dense structure of the SiO₂/PMMA coating layer.

This improvement in the C-rate capability of the SiO₂/PMMA-BNP composite separator can be further confirmed by examining the ionic conductivity. The results in Fig. 5a and b show that the ionic conductivity ($=0.74 \text{ mS cm}^{-1}$) of the SiO₂/PMMA-BNP composite separator is higher than that ($=0.48 \text{ mS cm}^{-1}$) of the SiO₂/PMMA composite separator. The higher ionic conductivity of the SiO₂/PMMA-BNP composite separator demonstrates that the porous structure in the coating layer is highly developed, and therefore contributes to facile lithium-ion diffusion after being filled with liquid electrolyte. Schematic illustrations of the structure and ionic transport of the composite separators are also given in Fig. 5. The bold arrow in the SiO₂/PMMA-BNP composite separator signifies relatively superior ionic transport. In future studies, the effects of ceramic composite coating layers on other aspects of electrochemical performance, including the cycleability of cells charged to various cut-off voltages, will be investigated.

4. Conclusions

SiO₂/PMMA-BNP composite separators have noticeably improved the cell performance, compared with conventional

SiO₂/PMMA composite separators. The SiO₂/PMMA-BNP coating layer features a highly porous structure, i.e., well-connected interstitial voids between close-packed binary nanoparticles. This novel morphology allows favourable liquid electrolyte wettability and facile ionic conduction, which play an important role in improving the discharge capacity and C-rate capability of cells. This study provides a new insight into the nanostructure control of ceramic composite separators, which are attracting interest for application in lithium-ion batteries that require enhanced safety and high-power density.

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