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Positive Effects of E-Beam Irradiation in Inorganic Particle Based Separators for Lithium-Ion Battery

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An inorganic separator was prepared by coating inorganic submicrometer sized particles on a nonwoven matrix followed by an E-beam irradiation treatment. Its characteristics were investigated by scanning electron microscopy, tensile strength analysis, thermogravimetric analysis, ionic conductivity measurements, and charge–discharge analysis. The mechanical and thermal properties of the separator were greatly enhanced by the simple curing under E-beam irradiation. However, there was no significant change in the morphology or ionic conductivity of the E-beam treated separator.
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Due to the growing energy storage needs for portable electronic devices and hybrid vehicles, as well as the potential market for electrical vehicles in the future, there is an increasing demand for high performance electrochemical energy sources such as batteries and fuel cells.[1-5] In the Li-ion battery system, the separator is a porous membrane placed between electrodes of opposite polarity, permeable to ionic flow but preventing electric contact of the electrodes.[6,7] In most batteries, the separators are either made of nonwoven fabrics or microporous polymeric films such as polyethylene, polypropylene, and poly(tetrafluoroethylene).[7] Polymer based separators soften or melt when the temperature reaches 130°C or higher because of their dimensional instability, which may cause internal short-circuiting or lead to thermal runaway.[8] Therefore, it is necessary to design an alternative separator, which has dimensional stability at a high temperature. Among the possible alternative separators, the current gel materials with inorganic nanoparticles might perform well from an electrochemical point of view, but they have several drawbacks from the viewpoint of their safety and handling.[9] For these reasons, another alternative type of separator was introduced for use in rechargeable Li-ion batteries.[10,11] These separators were made of inorganic submicrometer sized particles and a small amount of polymer binder. These inorganic particle based separators showed excellent thermal stability as well as wettability, but they have insufficient mechanical strength to withstand the handling procedures used during cell winding assembly.[12] Kritzer introduced nonwoven support materials to improve the mechanical strength of inorganic based separators.[12] Recently, nonwoven supported inorganic separator prepared from a sol–gel coating method was commercialized for a Li-ion battery by Degussa (SEPARION). However, the practical application of the inorganic particle coated nonwoven separator by using polymeric binder has still not been realized because the mechanical strength of these inorganic based membranes with nonwoven supports is insufficient for the roll-to-roll process.

Herein, we report a simple method of preparing inorganic particle based separators with enhanced mechanical and thermal properties. The primary results show that the above drawback of the inorganic separators is solved by treatment with E-beam illumination. E-beam technology is a very effective method to induce graft polymerization or cross-linking because the high density of the E-beams can create a large amount of radicals over entire samples.[13,14]

Experimental

The inorganic particle based separator was prepared as follows: 400 nm Al_2O_3 (Sumitomo Chem. Co.) powders were dispersed in xylene solvent (Aldrich Co.) with a surfactant [3-(trimethoxysilyl) propylmethacrylate, Aldrich] and then heated at 130°C for 24 h. After the filtering process, the particles were washed with xylene and ethanol. The weighed Al_2O_3 powder and poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) (Kynar 2801, Arkema Co.) were dispersed in acetone solvent and ground for 3 h using a homogenizer. In this work, the typical compositions of the separator were between 80:20 and 95:5 (by weight) Al_2O_3/PVDF-HFP. Then, the 20 μm thick nonwoven matrix (Aramid fiber, wet-laid, weight 1 mg/cm²) was dipped into the solution for 1 s and dried in a chamber for 5 min (humidity 30%, temperature 20°C). Then the samples were dried again under atmosphere condition for 24 h. When the composition of the separator was 90:10 (by weight) Al_2O_3/PVDF-HFP, the mass fraction of nonwoven was about 0.3. The thickness of the inorganic separator was controlled in the range of 20–25 μm by adjusting the viscosity of the suspension. The prepared separators were then irradiated by an E-beam at doses of 50 K and 100 kGy at a dose rate of 10 kGy/pass at room temperature to cross-link the PVDF-HFP binder material in the inorganic nanoparticle based separator. UV-cured inorganic based separators with the 10 wt % binder content [PVDF-HFP:poly(ethylene glycol) diacrylate (PEGDA)=5:5 with a small amount of a photoinitiator] were also prepared and UV-cured under UV irradiation (Sankyo Denki) for 4 h.

The morphology of the separator was examined by scanning electron microscope (SEM, JSM-7000 F, Japan). Thermogravimetric analysis (TGA 6100, Seiko Instruments, Japan) was used to evaluate the thermal properties of the separators. They were heated from 30 to 400°C at a heating rate of 10°C/min under a N_2 atmosphere. The mechanical properties of the separators were determined using a universal tensile machine (Nexygen Plus model LR30K tester, Lloyd Instruments, England). The test specimens were 6 mm wide and approximately 30 μm thick. The grip distance was 50 mm and the cross-head speed was 10 mm/min.

The anode had a composition of 94 wt % graphitized mesocarbon microbeads (MCBM2528) and 6 wt % Kynar 741 as a polymeric binder. The cathode was composed of 90 wt % $LiCoO_2$, 6 wt % Super-P, and 4 wt % PVDF. The electrolyte for the bicell (2 × 2 cm) was $LiPF_6$ (1 M) with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (1:1:1. v/v/v, Techno SEMICHEM Co., Ltd., Korea). The charge–discharge tests of the cells were performed using a TOSCAT-3000U (Toyo System Co., Ltd.). The cells were charged up to 4.2 V at 0.2C rate and then discharged to 3.0 V at various C-rates. The charge process was cut off at 20% of the initial constant current.

The ionic conductivity of the separators activated with electrolyte solution at room temperature was determined by the ac imped-
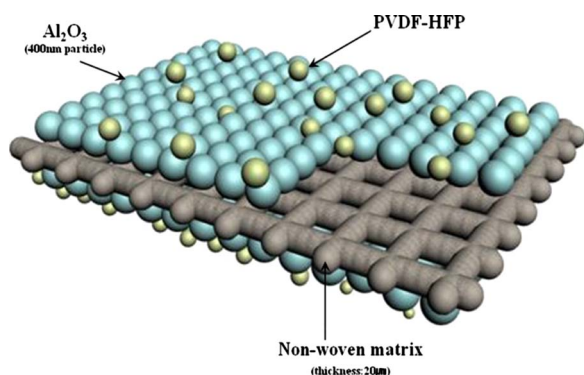
Figure 1. (Color online) A schematic diagram of the proposed inorganic nanoparticulate separators.

ance technique over the frequency range from 0.01 to 100 kHz using a CHI-660 (CH Instruments, Austin, TX). The constant potential was fixed at 5 mV. Samples with an area of A and thickness of L were sandwiched between two stainless steel blocking electrodes to measure the electrolyte resistance (R_b). The conductivity was then calculated from the following equation

$$\sigma = L/(R_b A) \qquad [1]$$

Results and Discussion

In the present study, an inorganic nanoparticle based separator was prepared by the direct coating of a nanoparticle dispersed solution onto the nonwoven matrix. This solution consisted of submicrometer sized Al_2O_3 and a small amount of PVDF-HFP binder. The ion-conducting polymeric binder material facilitates the interconnection between the Al_2O_3 particles and the ion transport. Figure 1 shows a schematic diagram of the proposed inorganic submicrometer sized particle based separators.

Figure 2a shows the morphology of the nonwoven matrix obtained by SEM observation. As shown in Fig. 2a, the separator contains polymeric fibers with a diameter of around 5–15 μm. Because the maximum pore size of the nonwoven matrix is larger than 100 μm, it is impossible to use the matrix itself as the separator of a Li-ion battery. However, this problem is overcome by filling the nonwoven matrix with 400 nm inorganic particles. The macropores in the nonwoven matrix were well filled with the inorganic particle/PVDF-HFP composite material with no significant defects, as shown in Fig. 2b. Because the prepared membrane is flexible and electrically isolating, Li-ion batteries can be prepared by the winding process. Figure 2c shows the inorganic particle/PVDF-HFP coated on the nonwoven matrix treated with E-beam irradiation at 100 kGy. As shown in Fig. 2c, the surface morphologies were not significantly influenced by the E-beam irradiation.

In Li-ion batteries, the essential role of the separator is to prevent electronic contact, while enabling ionic transport between the cathode and the anode. Recently, a new type of separator was introduced for use in rechargeable Li and Li-ion batteries.[10-12] The films were made of inorganic nanoparticles and a small amount of polymer binder. However, they do not have sufficient mechanical strength to commercialize.[12] For inorganic particle based separators, the mechanical strength tends to strongly depend on the adhesion force among the particles originating from the PVDF-HFP binder. Figure 3 shows the tensile strength values of the inorganic particle based separators with and without E-beam irradiation. The tensile strength value of the original separator was greatly improved through the E-beam irradiation treatment. Presumably, the cured PVDF-HFP molecules can enhance the interconnection force between the particles. When the cured PVDF-HFP was immersed in acetone, which is a good solvent for PVDF-HFP, it was not dissolved in the solvent. From this phenomenon, it can be concluded that the PVDF-HFP
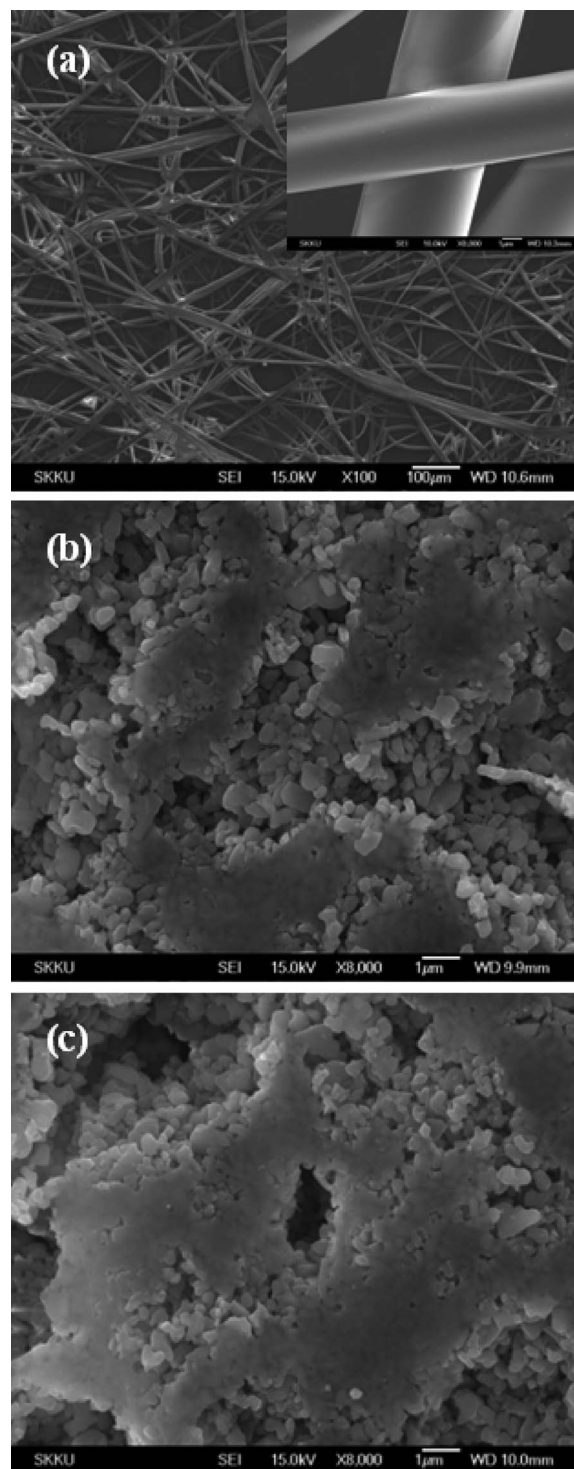

Figure 2. SEM micrographs of the surfaces of the (a) nonwoven matrix and inorganic separators with (b) Al_2O_3/PVDF-HFP (9:1 by weight) and (c) E-beam cured Al_2O_3/PVDF-HFP (9:1 by weight) using 100 kGy.

molecules were cross-linked by the E-beam treatment.[15] As a result, the drawback of the inorganic particle based separator mentioned above could be solved by the simple treatment method proposed herein.

As mentioned above, the inorganic particle based separator has significantly enhanced thermal properties because the main material in the separator is Al_2O_3 submicrometer particles. However, the thermal melting or degradation of the polymeric binder in the inor-
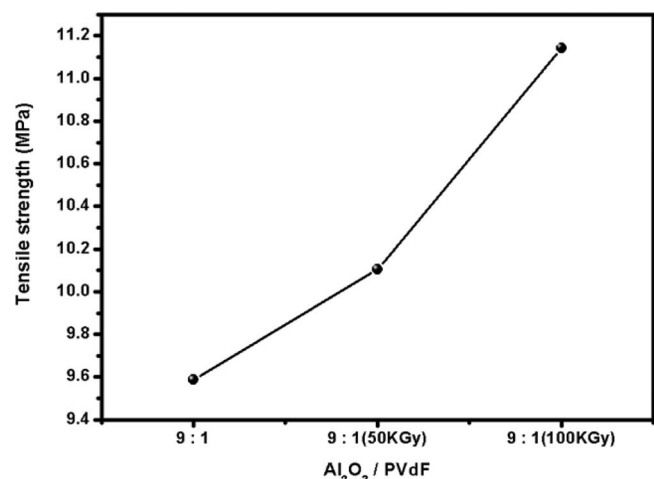
Figure 3. Mechanical properties of inorganic separators with Al$_2$O$_3$/PVDF-HFP (9:1 by weight) and E-beam cured Al$_2$O$_3$/PVDF-HFP (9:1 by weight) using 50 kGy and E-beam cured Al$_2$O$_3$/PVDF-HFP (9:1 by weight) using 100 kGy.

Figure 5. Mechanical properties as a function of PVDF contents in Al$_2$O$_3$/PVDF-HFP membrane with and without irradiation.

ganic separator is still an important issue to consider when evaluating the thermal stability of the separator for Li-ion batteries. Generally, cross-linked polymers show greatly enhanced thermal stability compared with linear polymers. Therefore, the more enhanced thermal stability of the inorganic separator subjected to E-beam irradiation was to be expected. Figure 4 shows the TGA curves for the Al$_2$O$_3$/PVDF-HFP separator treated with different E-beam treatment conditions. The noticeable weight loss of the original inorganic separator started at around 270°C. The weight loss corresponds to the decomposition of PVDF-HFP because the weight percent of the nonwoven matrix in the composite separator is negligible. Even though the ratio of Al$_2$O$_3$ to PVDF-HFP in the mixture solution was fixed at 9:1, the coated membrane seems to have a PVDF-HFP content of 30 wt %. The E-beam treated inorganic separators did not show any weight loss up to 400°C.

Figure 5 shows the tensile strengths of the inorganic separators containing various amounts of PVDF-HFP with and without E-beam treatment (100 kGy). The tensile strength of neat nonwoven was about 9.5 MPa. All of the samples subjected to E-beam irradiation showed enhanced tensile strength behavior compared with those
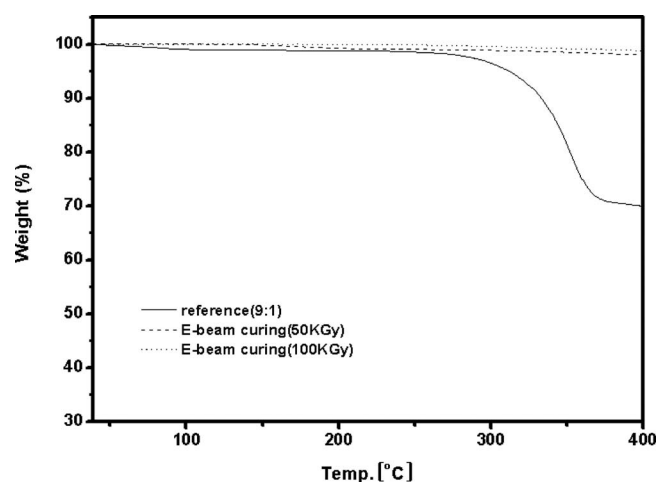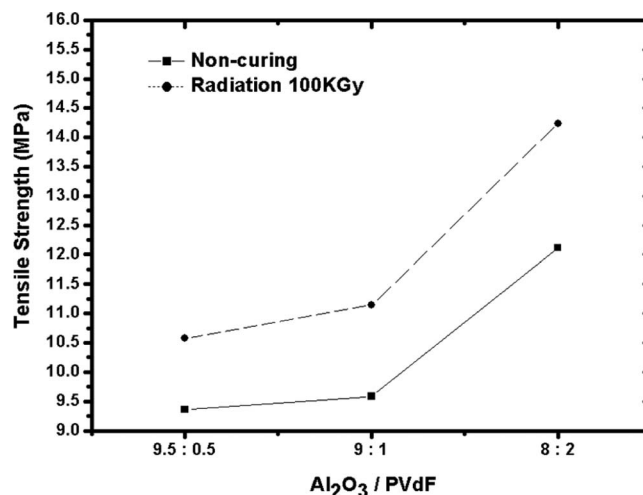
without E-beam treatment. With increasing binder content, the tensile strength was also gradually increased. Moreover, the tensile strength of the irradiated separator with an Al$_2$O$_3$ to PVDF-HFP ratio of 9.5:0.5 was about 10.5% higher than that of the same separator without E-beam treatment, whereas the tensile strength of the irradiated separator with an Al$_2$O$_3$ to PVDF-HFP ratio of 8:2 was 17% higher than that of the corresponding separator without E-beam treatment. From these results, it can be seen that the enhancement of the mechanical strength of the inorganic based separator is strongly influenced by the binder content.

Figure 6 shows the TGA curves for the inorganic based separators with the E-beam curing step but with different binder contents. The total weight losses of all of the samples are less than 2% above 400°C. From Fig. 4, a noticeable weight loss was first observed at around 280°C, resulting from the degradation of PVDF-HFP. Therefore, the results from Fig. 6 indicate that all of the PVDF-HFP, even in the separator with an Al$_2$O$_3$ to PVDF-HFP ratio of 8:2, is fully cross-linked when irradiated under 100 kGy conditions.

Figure 7 shows the ionic conductivity of the various separators with different binder contents measured at room temperature as a function of the amount of irradiation. It can be seen that the conductivities of all of the samples have similar values. The cured PVDF-HFP molecules are not expected to be able to uptake the electrolyte. Therefore, the retention of the ion conductivity of the
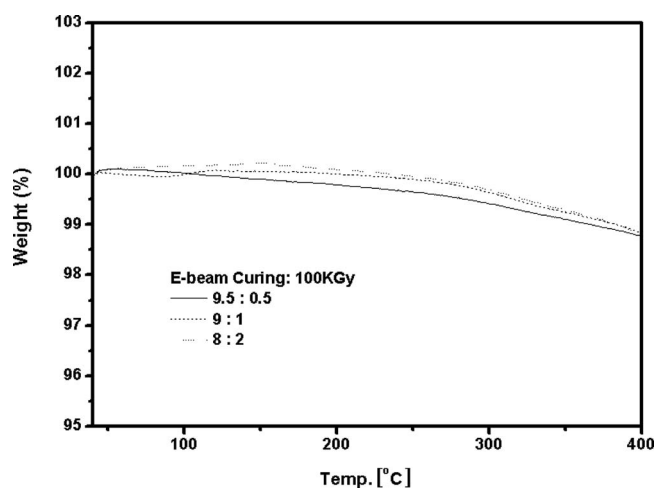

Figure 4. Thermogravimetric curves of inorganic separators with (——) Al$_2$O$_3$/PVDF-HFP (9:1 by weight) and (- - - -) E-beam cured Al$_2$O$_3$/PVDF-HFP (9:1 by weight) using 50 kGy and (·····) E-beam cured Al$_2$O$_3$/PVDF-HFP (9:1 by weight) using 100 kGy.

Figure 6. Thermogravimetric curves of E-beam cured inorganic separators with different Al$_2$O$_3$/PVDF-HFP ratios.
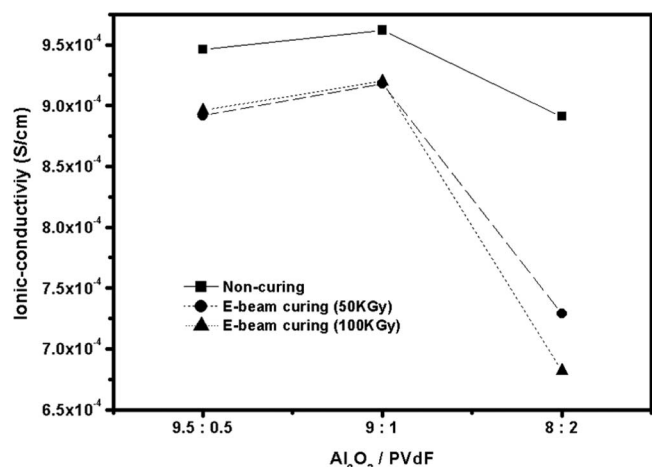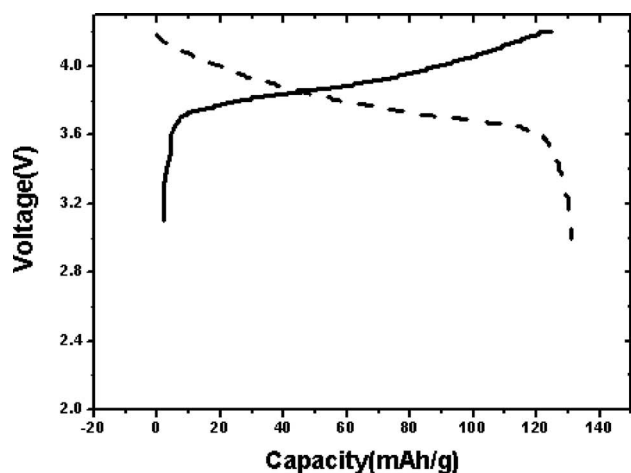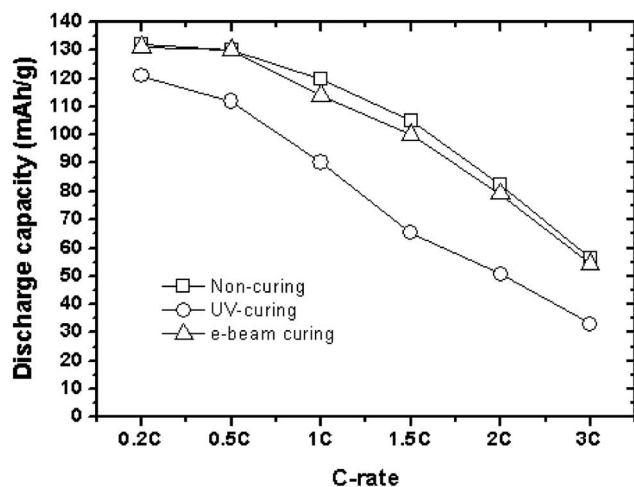
Figure 7. Effect of E-beam curing on the ionic conductivity as a function of the Al_2O_3/PVDF-HFP ratio.

(a)

(b)

Figure 8. (a) Representative charge/discharge curves of the unit cell with E-beam cured inorganic based separator (Al_2O_3/PVDF-HFP of 9:1) and (b) results of the rate capability test for the cells.

separators, even those treated with E-beam irradiation, indicates that voids among the Al_2O_3 particles are the main ion transporting paths resulting in good ionic conductivity.

The charge–discharge profiles of the unit cell at rates of 0.2C are given in Fig. 8a. The intercalation of the lithium cations in $LiCoO_2$ gives rise to a voltage plateau at about 3.8 V. It is evident from Fig. 8b that the E-beam treatment does not affect the cell performance significantly. The capacity decrease slope of the cell with the inorganic separator treated with E-beam irradiation was almost the same as that of the cell with the neat inorganic separator. This result agrees well with the behavior of the ionic conductivity. To compare the E-beam cured system with the UV-cured system, UV-cured inorganic based separators with the same binder content (PVDF-HFP:PEGDA = 5:5 with a small amount of a photoinitiator) were also prepared, and the corresponding results are presented in Fig. 8b.[16] As shown in Fig. 8b, the UV-cured system showed worse C-rate behavior than the E-beam cured system. This might be due to the negative effect of the uncured PEGDA oligomer or residual photoinitiator in the separator.

Conclusions

The mechanical and thermal properties of an inorganic based separator, which was composed of Al_2O_3 submicrometer sized particles and a small amount of polymeric binder, were greatly improved by the simple E-beam curing method. However, compared with the pure inorganic separator, there was no significant change in the morphology or ionic conductivity of the E-beam cured separator. As the volumetric cell capacity is increased, the safety issues of the Li-ion battery will increase in importance. It is believed that one of the possible solutions to this problem would be to replace the current polyolefin based separators with inorganic based separators. The inorganic based separator prepared from a simple Al_2O_3 submicrometer sized particles on the nonwoven supported by a small amount of polymeric binder might have several advantages compared to the SEPARION product. The proposed simple method can solve several drawbacks of the inorganic based separator, suggesting good promise for its practical application.

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