

Full Length Article

Electron beam induced strong organic/inorganic grafting for thermally stable lithium-ion battery separators



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ABSTRACT

A tailored interface between organic and inorganic materials is of great importance to maximize the synergistic effects from hybridization. Polyethylene separators over-coated with inorganic thin films are the state-of-the-art technology for preparing various secondary batteries with high safety. Unfortunately, the organic/inorganic hybrid separators have the drawback of a non-ideal interface, thus causing poor thermal/dimensional stability. Here, we report a straightforward method to resolve the drawback of the non-ideal interface between vapor deposited SiO₂ and polyethylene separators, to produce a highly stable lithium-ion battery separator through strong chemical linking generated by direct electron beam irradiation. The simple treatment with an electron beam with an optimized dose generates thermally stable polymer separators, which may enhance battery safety under high-temperature conditions. Additionally, the newly formed Si–O–C or Si–CH₃ chemical bonding enhances electrolyte-separator compatibility and thus may provide a better environment for ionic transport between the cathode and anode, thereby leading to better charge/discharge behaviors.

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1. Introduction

With the rapidly growing industrial importance of high energy density in a limited space, for use in applications such as mobile electronic devices of various shapes and electric or hybrid-electric vehicles (EVs or HEVs) [1,2], emerging high energy density lithium-ion batteries with high operating potential and high capacity has been receiving increasing attention [3]. Various emerging cathode and anode materials with high specific/volumetric energy densities have been explored [4–7]. However, the main approach to enhancing the energy density of lithium-ion batteries in terms of the separators (porous membranes) is simply to decrease the film thickness of polyethylene (PE) or polypropylene (PP), because these porous polymer films are not directly related to specific/volumetric energy density. Inherently, the thermal and dimensional stability of the polymeric porous film also decreases dramatically with decreasing film thickness; this characteristic has led to serious concerns about the safety issues of lithium-ion batteries, such as possible explosion and burning under high temperature or hard internal shorting between electrodes [8].

From the viewpoint of the basic requirements of battery separators, such as uniform pore size, high tensile strength, and chemical stability [9,10], ultra-thin polymeric separators coated with inorganic insulating particles, such as SiO₂ and Al₂O₃, allow easy integration into highly packed batteries with high energy density without raising safety concerns [11]. However, the additional inorganic particle layer on the PE separator with a thickness of approximately 3–6 μm decreases the volumetric energy density of the cells [12–14]. To increase the volumetric energy density of lithium-ion batteries, a new integration method of inorganic material into the PE separator is highly desirable. To overcome the drawback of conventional inorganic insulating particles coating PE separators and to improve the dimensional stability of the PE separator, alternative thin-film deposition of an inorganic layer inside the pores of a PE separator from atomic layer deposition (ALD), chemical vapor deposition (CVD) and sputtering methods have previously been suggested [15–17]. Although gas or vapor-phase deposition allows for enhanced thermal and dimensional stability, it is not guaranteed that the inorganic layer will be completely anchored on the surface of the PE separator, thus potentially weakening the positive effects of the inorganic layer and inducing delamination of the inorganic layer from PE during long-term cycling.

The porous structure of commercially available PE separators with sub-micron-sized channels is suitable for introducing thin

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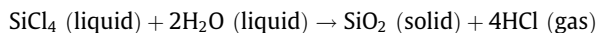
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SiO₂ film by chemical vapor deposition, from which more enhanced thermal and dimensional stability can be obtained [18,19]. In the present work, we report that controlled electron beam irradiation is able to cross-link PE and inorganic thin film together (Fig. 1), thus resulting in greatly improved thermal and dimensional stability of the PE separator. The poor thermal and dimensional stability of commercially available PE separators could not be resolved via a thin inorganic coating layer, owing to insufficient adhesion of the inorganic coating layer on the PE surface; however, high energy from electron beam irradiation generates additional covalent bonding between the organic polymer and the inorganic thin film, thereby enhancing the thermal stability of commercial PE separators (Fig. S1). Moreover, the SiO₂-coated PE separator with covalent bonding generated by the electron beam treatment exhibits greatly improved affinity for a liquid electrolyte, thereby dramatically increasing the C-rate battery performance.

2. Experimental section

2.1. Preparation of the SiO₂-grafted PE separator

A PE separator (T16-518, 16 μm thickness, SK energy) was used as the substrate. The SiO₂-grafted PE separator was fabricated through the following chemical vapor deposition method. First, the PE separator was surface treated with O₂ plasma (Harrick plasma) for 3 min. Then, the PE separator was placed in a chamber filled with saturated water vapor for several minutes to dose water vapor on the PE separator. These conditions were suitable for chemical reaction with silicon tetrachloride (SiCl₄, 11%, Aldrich). The evaporated SiCl₄ vapor at 70 °C in the other chamber reacted with the adsorbed water layer on the PE separator.



Then, the SiO₂ deposited PE separator was irradiated with an electron beam with 0, 5, 10, 20 and 30 kGy (1 Gy = 1 J kg⁻¹) doses at a dose rate of 10 kGy/pass at room temperature air condition with an electron accelerator (1.14 MeV, EB Tech, Korea). Finally, the SiO₂-grafted PE separator was fabricated.

2.2. Characterization

The surface functionalities of the SiO₂-grafted PE separator were analyzed with FT-IR spectroscopy (Vertex 70, Bruker) in the wavenumber range of 1800–500 cm⁻¹ at 4 cm⁻¹ resolution with

32 scans in TR mode. The morphology of the separators was observed with field emission scanning electron microscopy (FE-SEM, JEOL 7800F), and the C/O/Si ratio was detected by energy dispersive X-ray spectroscopy (EDX, JEOL 7800F). Moreover, the contact angle was obtained by dropping distilled water. The thermal shrinkage of the SiO₂-grafted PE separators was measured as the dimensional change after 140 and 150 °C for 0.5 h. The degree of thermal shrinkage was calculated with the following equation.

$$\text{Shrinkage (\%)} = \frac{W_i - W_f}{W_i} \times 100$$

W_i and W_f are the initial and final areas, respectively, of the separator. The wetting ability test of the separators was conducted in 1 M LiPF₆ with ethylene carbonate (EC)/diethylene carbonate (DEC)/ethyl-methyl carbonate (EMC) (1:1:1, v/v/v) for 1 h.

2.3. Electrochemical measurement

Stainless steel (working electrode) and lithium foil (counter and reference electrode) were used to analyze the linear sweep voltammetry. The measurement range of voltage was between 2.0 and 6.0 V (vs. Li/Li⁺) at a scan rate of 1 mV s⁻¹. The following equation was used to calculate the ionic conductivity (σ), where d is the thickness of the separators, R_b is the bulk resistance, and S is the area of the separators.

$$\sigma = d / (R_b \times S)$$

The R_b was analyzed through electrochemical impedance spectroscopy (EIS, Ivium Compactstat) at an amplitude of 5 mA and a frequency range between 100 mHz and 1 MHz. The electrochemical performance of the separators was examined with 2032 coin-type full cells, with the separator sandwiched between a graphitized mesocarbon microbead (MCMB2528) anode and a LiCoO₂ cathode and soaked with electrolyte composed of 1 M LiPF₆ with ethylene carbonate (EC)/diethylene carbonate (DEC)/ethyl-methyl carbonate (EMC) (1:1:1, v/v/v). The anode was composed of 94 wt.% MCMB and 6 wt.% Kynar 741 as a polymeric binder. The cathode had 90 wt.% LiCoO₂, 6 wt.% Super-P and 4 wt.% PVDF. For the charge-discharge tests, the cells were charged up to 4.3 V at a rate of 0.2 C and then discharged to 3.0 V at various C-rates. A cycle test was conducted at a charge/discharge current density of 0.5 C/0.5 C.

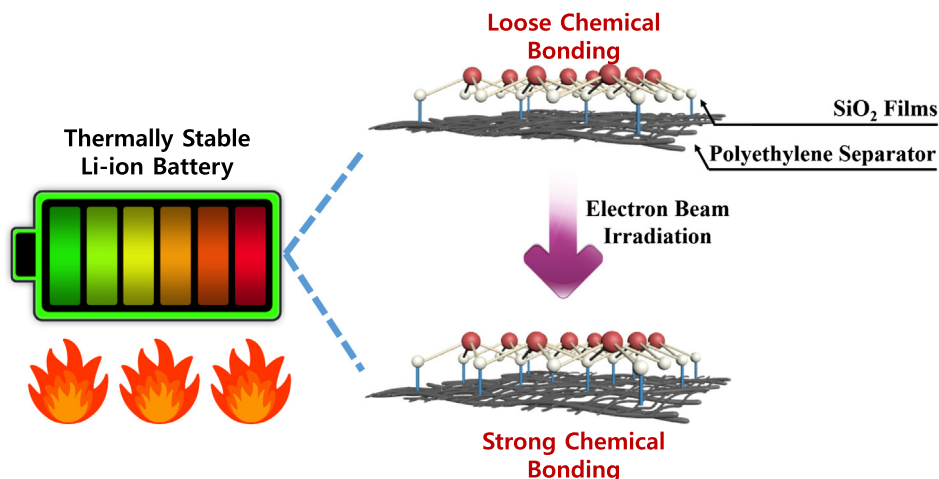


Fig. 1. Scheme of the SiO₂/PE separator before (Top) and after (Bottom) treatment with the electron beam irradiation process (EB-SiO₂/PE separator).

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