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Flame retardant coated polyolefin separators for the safety of lithium ion batteries

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Abstract−A thermally stable and flame-retardant separator is proposed to improve the safety of lithium ion batteries. The separator is prepared by dip-coating both sides of a conventional tri-layer polyolefin separator with brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO). Significantly reduced thermal shrinkage and flammability are exhibited without decreases in the pore size or porosity of the conventional separator. By using the BPPO-coated separator, an electrochemical half-cell composed of a lithium metal anode and a $LiCoO_2$ cathode are successively tested. The resulting stable cycle performances are demonstrated. It is expected that the BPPO-coated separator can be a capable candidate as a separator for the safe of lithium ion batteries.

Keywords: Lithium Ion Batteries, Separator, Safety, Thermal Stability, Flame Retardant

INTRODUCTION

Lithium ion batteries, one of many sustainable energy systems, have attracted significant attention due to their high energy density and non-toxicity [1,2]. However, some explosive accidents with lithium ion batteries in laptops and mobile phones have been reported [3]. One of the reasons for the explosions is the appearance of deformation of the separator, which allows the transportation of lithium ions and the electrical separation of anodes and cathodes. Most separators sufficiently maintain their appearance at usual cell temperatures during charge/discharge operations. However, extreme conditions, such as flame attack, exposure to combustive temperatures, and long-term cycle operation, elevate cell temperature, leading to shrinkage and defects of the separators [4,5]. Such physical changes to the separators induce contact between anodes and cathodes, followed by the formation of a short circuit and overcharge, leading to a steeply increased cell temperature. When the temperature reaches the ignition point (the temperature of spontaneous combustion), a fire or explosion may occur. To prevent these problems, researches on improving the thermal resistance of separators have been actively conducted, such as ceramic coating, inorganic-organic composite separator preparation, and functional polymer grafting [6-8].

In our previous work [9], a flame retarding separator was prepared using brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) by a vapor-liquid phase inversion method. BPPO has a strong potential as a thermally stable and flame retarding separator due to its structure, which consists of benzene rings and bromines. The benzene ring enhances the thermal stability because its carbon and hydrogen bonds adsorb heat energy. Bromine decreases flammability because the bromine radicals act as scavengers during combustion [10-12]. Indeed, the prepared BPPO monolayer separator in the previous work showed remarkably reduced flammability and improved thermal stability without any decrease in cell performance. However, the separator was unable to shut the battery down at a high temperature (>135 °C) due to the too rigid structure of BPPO, even though the shutdown function is very important in lithium ion batteries. Another disadvantage of the BPPO monolayer separator is its complicated preparation process. The BPPO monolayer separator was prepared by the casting of a polymer slurry, which was prepared using BPPO and two types of organic solvents. The cast separator was kept in a nitrogen atmosphere and then soaked in deionized water for the phase inversion step. Afterwards, the BPPO monolayer separator was dried in an oven at 80 °C to evaporate water. For this reason, the present work was carried out to solve these disadvantages.

In this study, we have extended our previous work on the preparation process and thermal stability. As demonstrated previously, BPPO has remarkable features in terms of flame retardant and thermal stability. Polyolefin (i.e., polyethylene and polypropylene) separators have excellent meltdown and shutdown functions [13]. To simultaneously achieve the features of the BPPO and conventional polyolefin separators, BPPO-coated polyolefin separators have been prepared by a simple and material-saving process. Thermal shrinkage and flammability have been investigated to confirm the effects of the BPPO-coated separator. The successive cycle performances of the lithium ion battery assembled with the BPPO-coated separator and a conventional separator have been discussed.

EXPERIMENTAL

1. Preparation of the BPPO-coated Separator

BPPO (Tianyi International Corporation) was dissolved in chloroform (Fisher Scientific) for preparing the 11.88 wt% BPPO slurry. A conventional tri-layer polyolefin separator (Celgard® 2340, PP/PE/PP layers, porosity: 40%, pore size: 0.035 μm, thickness: 38 μm)

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was then immersed in the BPPO slurry for 1 min to allow for sufficient permeation into the pores. Afterwards, the separator was withdrawn at a rate of 8.56 mm/min using a dip coater (KSV-DC, KSV Instruments Ltd.).

2. Physical Analysis

The presence of BPPO on the prepared separator was investigated by using Fourier transform infrared spectrometry (FT-IR, 460 Plus, Jasco) within 650 to 4,000 cm^{-1} of the wavenumber range. The pore size and cross-sectional thickness of the BPPO-coated separator were analyzed by scanning electron microscopy (SEM, JEOL). Porosity was measured using a mineral oil (Sigma-Aldrich) by weighing the oil uptake [14], and air permeability was examined with a digital bubble meter (Digital Flowmeter Model 4074, Alltech) by applying air at a constant pressure in a perpendicular (thickness) direction [15].

3. Thermal Stability and Flame-retardant Analysis

Thermal shrinkage was evaluated by applying high temperatures to the 4 cm×4 cm separators within the temperature range of 100 to 180 °C at 20 °C intervals for 30 min, respectively. The deformed size of the separators was measured in longitude and transverse directions [16,17]. For the flammability test, the separators were sufficiently wetted by 1 M $LiPF_6$ EC/DEC (1/1 by volume) electrolyte. The wetted 3 cm×3 cm separators were then flamed by using an alcohol lamp. The process of burning the separators was captured on a video camera until the fire ceased [18].

4. Electrochemical Cell Test

The cycle performance of the lithium ion cells was examined by assembling a CR2032-type coin cell using a lithium metal anode and a $LiCoO_2$ cathode with 1 M $LiPF_6$ in EC/DEC (1/1 by volume, PANAX E-Tec Co., Ltd.) electrolyte. The assembly of the cells was conducted in an argon gas-filled glove box. The cycle performances of the lithium ion cells were evaluated within the voltage range of 3.0-4.2 V at a rate of 0.1 C using an automatic battery cycler (WBCS3000, WonATech), while measuring the relative and charge/discharge capacities.

RESULTS AND DISCUSSION

1. Physical Properties

The presence of BPPO on the separator was confirmed by analyzing FT-IR, as presented in Fig. 1. Three types of separators, including the conventional separator, BPPO-coated separator, and BPPO film, were compared. The conventional separator and BPPO film showed peculiar peaks. Meanwhile, the BPPO-coated separator revealed the combined peaks of the conventional separator and BPPO film. The dotted line indicates the duplicated peaks in the BPPO-coated separator. Therefore, the result demonstrated that BPPO was successfully layered on the conventional separator using the dip-coating technique, meaning that the BPPO-coated separator possesses the conventional separator and BPPO properties.

The separator thickness before and after BPPO coating was 38 μm, which implies that BPPO was layered on the conventional separator less than 1 μm thick. As the thickness of the separator influences the lithium ion transport in cells, thin separators are generally preferred. In this regard, the dip-coating conditions are significantly important for forming the thin layer. The dip-coating technique, as based on the capillary theory, forms a layer on the surface through three steps: immersion, formation, and evaporation. The loading amount and coating thickness are determined by the polymer slurry viscosity, the dipping and withdrawing rates, the number of coatings, the evaporation rate of solvents, and the drying conditions [19,20]. Therefore, thin layers for preserving the pore size and porosity of the conventional separator could be formed under the condi-

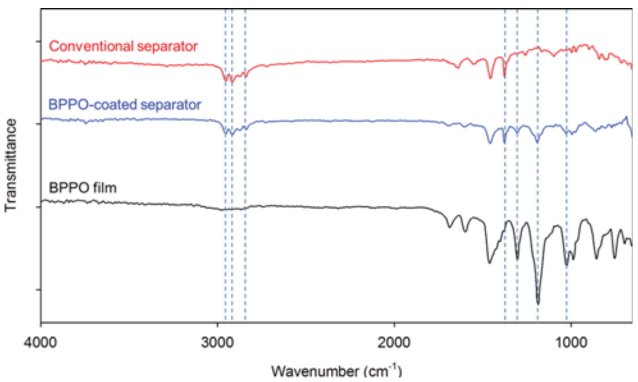

Fig. 1. FT-IR results of the conventional separator, BPPO-coated separator, and BPPO film.

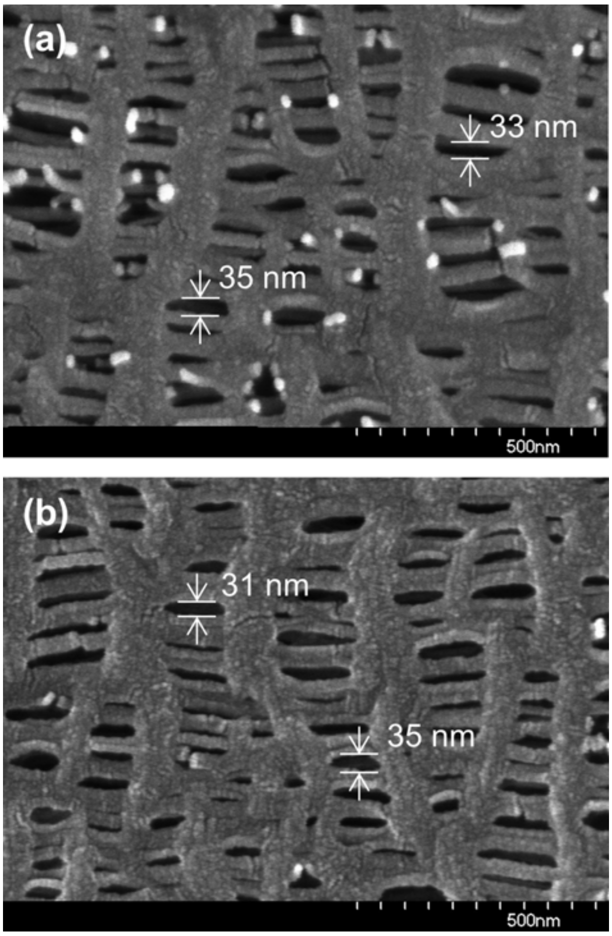

Fig. 2. SEM images of (a) the conventional separator and (b) BPPO-coated separator surfaces.

tions of the low polymer slurry viscosity, the rapid evaporation rate of the solvent at an ambient temperature, and the slow withdrawal rate.

In Figs. 2(a) and (b), the images show the morphologies of the conventional separator and the BPPO-coated separator surfaces, respectively. Fig. 2(b) reveals a rougher surface than that of the conventional separator due to the embedded BPPO, exhibiting similar pore sizes. According to the porosity measurement and the results of the air permeability test, the conventional separator exhibited 31.1% porosity and a Gurley value of 139.2 s/100 cc; the BPPO-coated separator presented 31.8% porosity and a Gurley value of 144.2 s/100 cc. This indicates that the pores, porosity, and tortuosity of the BPPO-coated separator were well preserved compared to the conventional separator.

2. Thermal Stability and Flame-retardant Analysis

Thermal shrinkage was investigated to prove the thermal stability of the BPPO-coated separator. Fig. 3(a) presents the external appearance of the separators before and after the shrinkage test at 160 °C for 30 min. The separators at an ambient temperature showed colored surfaces. After the heat treatment, the two separators became transparent, which implies that the pores in the separators were closed by the shutdown effect [21]. Fig. 3(b) exhibits the ratio of the thermal shrinkage according to the temperatures. The dimensional shrinkage of the conventional separator was higher than that of the BPPO-coated separator at every temperature. The shrinkage ratio was suddenly changed at two points of 120 and 160 °C. The conventional separator consists of polyethylene and polypropylene, and their melting points are 135 and 165 °C, respectively [22]. Therefore, the rapid shrinkage points were observed near the melting points of the employed olefin polymers. The BPPO-coated separator also showed rapid change points at 120 and 160 °C. However, the decrement ratio was lower than the conventional separator because the coated BPPO kept the polyolefin separator appearance at high temperatures. Wu et al. presented the degradation point of BPPO as 260 °C, as determined by a thermogravimetric analysis (TGA) experiment [23]. Therefore, the BPPO-coated separator can be protected at a higher temperature than the commercial separator.

A flammability test was performed to prove the flame-retardant effect. Fig. 4 displays photographs of the process of testing the flammability of the separators containing the liquid electrolyte. The conventional separator was melted as soon as it touched the fire, and a part of the separator was segregated from the origin separator. After combustion was completed, there was nothing left. In contrast, the BPPO-coated separator was not divided from the origin separator

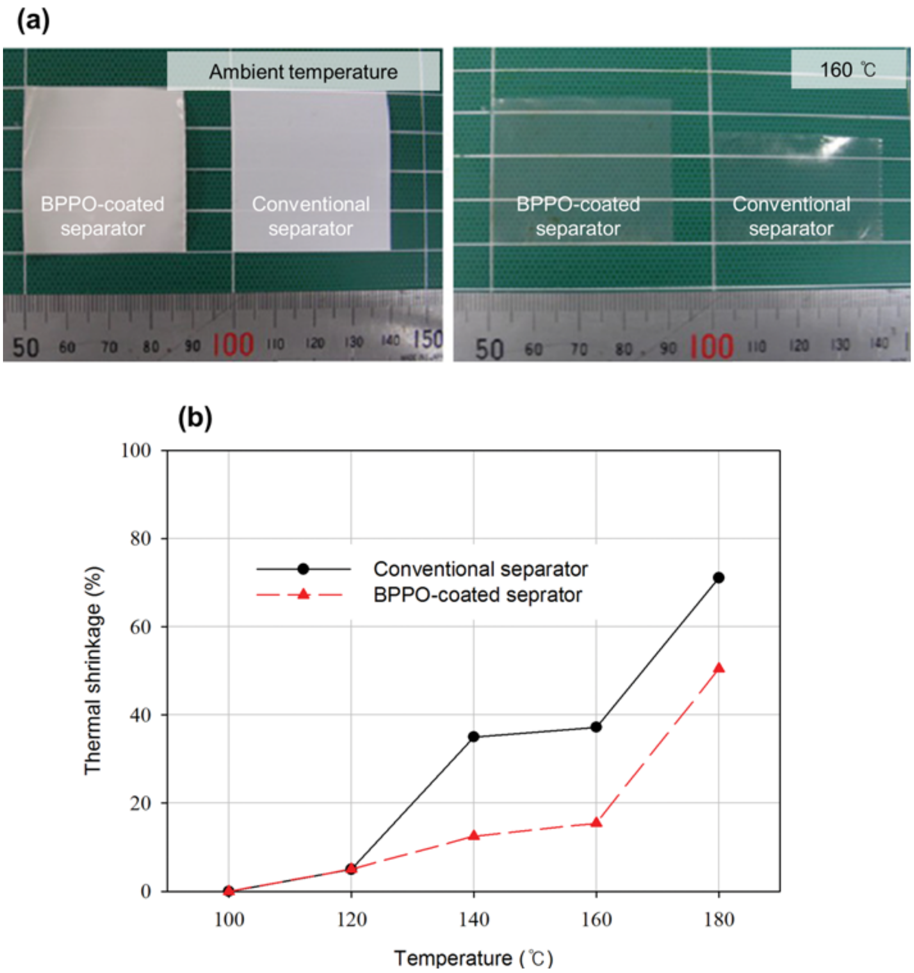

Fig. 3. (a) Photographs of the BPPO-coated separator and conventional separator before and after the heat treatment at 160 °C for 30 min, and (b) thermal shrinkage of the separators as a function of temperature.

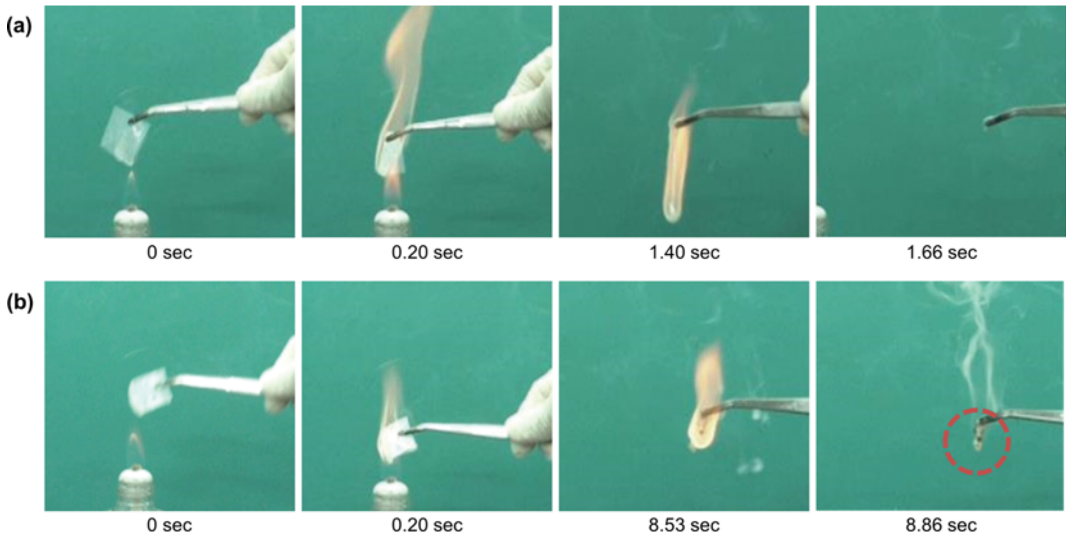

Fig. 4. Photographs of (a) the conventional separator and (b) BPPO-coated separator captured during the flammability test.

during combustion, and a part of the separator remained. It indicates incomplete combustion due to the coated BPPO, reducing the flammability of the separator. These tests clearly showed the improved safety behavior of the BPPO-coated separator.

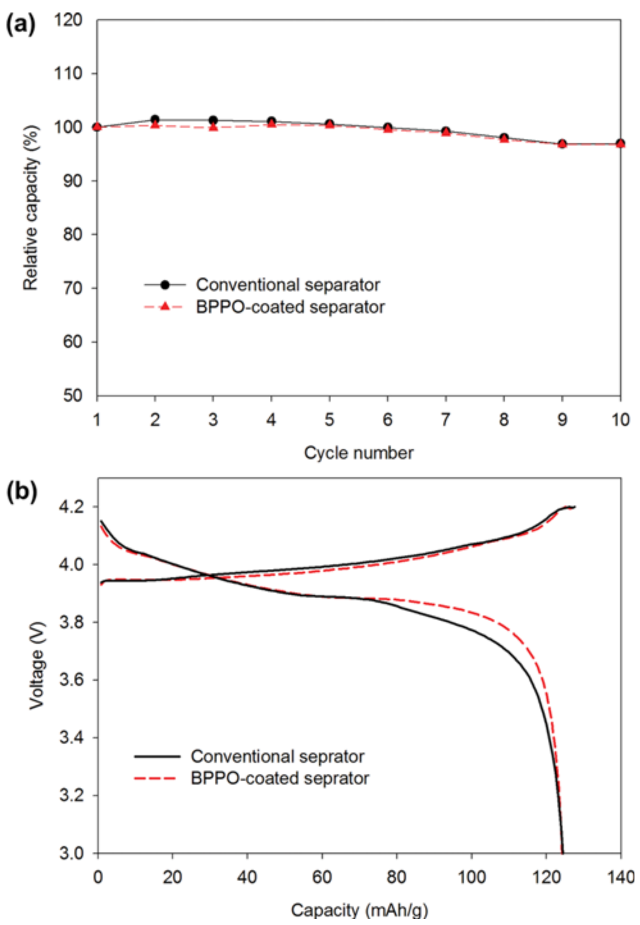

Fig. 5. (a) Relative capacities and (b) charge/discharge profiles at the tenth cycle of the cell assembled with the conventional separator or the BPPO-coated separator.

3. Cell Test

Cycle tests were conducted to obtain the charge and discharge capacities at 0.1 C in the voltage range of 3.0-4.2 V. Figs. 5(a) and (b) show the relative capacities during 10 cycles and the charge/discharge profiles at the tenth cycle, respectively. The relative capacity was obtained by using the discharge capacity ratio between the initial cycle and each cycle. The cell composed of the BPPO-coated separator had an initial discharge capacity of 128.4 mAh/g. After ten cycles, the discharge capacity of the cell diminished to 124.2 mAh/g, which corresponded to 96.8% of the initial discharge capacity. The discharge capacity of the conventional separator showed 128.3 mAh/g of the initial discharge capacity, and 97.0% of the relative capacity was retained after ten cycles. Such a similar operation efficiency proves that the BPPO-coated separator conducted the stable cycle operation without a disturbance to the lithium ion transportation.

CONCLUSIONS

A BPPO-coated separator was prepared to improve the flame-retardant ability and thermal stability of polyolefin tri-layer separators. Through the dip-coating process, the polymer slurry was simply coated on a conventional polyolefin separator, forming a layer less than 1 μm thick. According to the features of the BPPO and polyolefin separators, the BPPO-coated separator exhibited significantly improved thermal resistance and flame-retardant ability when compared to the pristine conventional separator. Furthermore, a stable successive cell performance was also confirmed. It is expected that the BPPO-coated separators may be useful for the safe of lithium ion batteries. The future development of separators will be done by using various polymers containing high bromine levels. The BPPO employed in this study is composed of 40 wt% bromine. Other commercial brominated polymers-polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA), and polybrominated biphenyl (PBBs)-

contain 48.5 to 75.5 wt% bromine. Therefore, more improved thermally stable and flame-retardant separators are expected through further work.

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