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Preparation of nanocomposite γ-Al_2O_3/polyethylene separator crosslinked by electron beam irradiation for lithium secondary battery

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ABSTRACT

Although micro-porous membranes made of polyethylene (PE) offer excellent mechanical strength and chemical stability, they exhibit large thermal shrinkage at high temperature, which causes a short circuit between positive and negative electrodes in cases of unusual heat generation. We tried to develop a new technology to reduce the thermal shrinkage of PE separators by introducing γ-Al_2O_3 particles treated with coupling agent on PE separators. Nanocomposite γ-Al_2O_3/PE separators were prepared by the dip coating of polyethylene(PE) separators in γ-Al_2O_3/poly(vinylidenefluoride-hexafluoropropylene) (PVDF-HFP)/crosslinker (1,3,5-trially-1,3,5-triazine-2,4,6(1 H,3 H,5 H)-trione (TTT) solution with humidity control followed by electron beam irradiation. γ-Al_2O_3/PVDF-HFP/TTT (95/5/2)-coated PE separator showed the highest electrolyte uptake (157%) and ionic conductivity (1.3 mS/cm). On the basis of the thermal shrinkage test, the nanocomposite γ-Al_2O_3/PE separators containing TTT irradiated by electron beam exhibited a higher thermal resistance. Moreover, a linear sweep voltammetry test showed that the irradiated nanocomposite γ-Al_2O_3/PE separators have electrochemical stabilities of up to 5.0 V. In a battery performance test, the coin cell assembled with γ-Al_2O_3/PVDF-HFP/TTT-coated PE separator showed excellent discharge cycle performance.

1. Introduction

Lithium-based batteries are widely used for portable electronics, mobile products and communication devices because of their higher energy density than other batteries (Takemura et al., 2005). A typical lithium ion battery consists of a positive electrode, a negative electrode, a separator, and a non-aqueous liquid electrolyte (Djian et al., 2007). A separator placed between a positive electrode and a negative electrode is one of the important components in rechargeable lithium batteries. It plays a crucial role in transporting ionic charge carriers between two electrodes and preventing the electric contact between two components (Arora et al., 2004). Thus, it requires higher mechanical, chemical, and electrochemical properties. Separators with enhanced thermal stability and good wettability in organic liquid electrolytes are desirable for the development of a safe and efficient lithium ion battery (Cho et al., 2007; Lee et al., 2009; Cheng et al., 2004).

Micro-porous polymeric membranes made of polyethylene (PE), polypropylene (PP), and laminates of PE and PP are widely used as separators in lithium-based non-aqueous batteries. Among them, PE membranes have been applied for separators of most lithium ion batteries (Kostecki et al., 2004). However, PE membranes shrink at high temperature, which may cause a short circuit between electrodes (Gwon et al., 2009). They also have a weakness of wettability towards electrolyte due to their inherent hydrophobic properties.

To improve the thermal property of polyolefin separators, polymer layers such as poly(vinylidene fluoride), poly(acrylonitrile) and poly(-methacrylate) or coating with inorganic powders such as SiO_2, Al_2O_3, TiO_2, MgO onto them have been studied. This approach has attracted increasing attention because of its effectiveness in improving wettability and preventing the thermal shrinkage (Dong et al., 2016; Chen et al., 2016; Song et al., 2012).

Although the coating process with inorganic particles is applied to polyolefin separators, mechanical breakdown of polyolefin is not avoidable in at temperature above the melting point of polyolefin. There have also been problems like the detachment between the coating layer and the polyolefin separator, and the separation of particles from coating materials as well as the agglomeration of inorganic particles. The inorganic particles have a strong tendency to undergo agglomeration followed by insufficient dispersal properties of the nanoparticles in polymer matrix.

Truong et al.(2010) investigated the dispersibility of silane-functionalized alumina nanoparticles in syndiotatic polypropylene. Yang et al.

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(2009) examined the surface properties of an untreated alumina and alumina treated with four types of coupling agents.

The use of ionizing radiation to modify polymers and to improve material properties is well known (Charlesby, 1960; Woods et al., 1994). For example, electron beam and gamma irradiation are widely used to crosslink PE such as cable and wire insulation, tubing, films, and fibers are sometimes irradiated at doses about 100 kGy to cause crosslinking of polymer chains to improve properties such as mechanical strength, thermal resistance, flame retardancy, and chemical resistance. After radiation crosslinking, the PE has significant gel content.

To increase affinity toward liquid electrolytes and lower the thermal shrinkage of PE separators, we used the new coating technology and radiation. To prepare the coating solution for PE separators, PVDF-HFP and TTT as a crosslinker were dissolved in acetone at room temperature. Surface-treated γ-Al$_2$O$_3$ was then put in this prepared solution. PE separators were dip-coated, and then dried under with humidity condition, followed by electron beam irradiation. γ-Al$_2$O$_3$ powders were treated with coupling agent to increase their dispersibility in coating solution. It is important that the coated layers of the separators have high porosity structures. There are several ways to prepare porous membranes, such as sintering, stretching, track etching and phase separation process (Lloyd et al., 1990). The phase separation process can be achieved by immersing the polymer solution in a non-solvent (diffusion induced phase separation). Non-solvent induced phase separation is the most common method for fabricating PVDF membranes with the desired porosity and pore structure. In this system, phase inversion is achieved under humidified conditions, that is, humidity acts as a non-solvent.

After coating process, radiation irradiation was employed to induce the crosslinking of coated layer and PE separator.

2. Experimental

2.1. Materials

A commercial microporous PE separator (SKLiBS, thickness: 12 μm) was supplied from SK Energy (Korea). Poly(vinylidenefluoride-hexafluoropropylene) (PVDF-HFP) and (1,3,5-trially-1,3,5-triazine-2,4,6(1 H,3 H,5 H)-trione (TTT) as a crosslinker were purchased from Aldrich and used as received. An electrolyte solution consisting of a 1.0 M of LiClO$_4$ in 1:1 (V/V) ethylene carbonate (EC) /diethyl carbonate (DEC) mixture was obtained from Techno-Semichem Co., Ltd. (Korea). γ-Al$_2$O$_3$ (size: 400 nm) was purchased from Buehler (USA). 3-(trimethoxysilyl)propylmethacrylate (TMSPMA) and xylene were obtained from Sigma-Aldrich. Other solvents were regent grade and used as received.

2.2. Preparation of *nanocomposite* γ-*Al$_2$O$_3$/PE separators*

γ-Al$_2$O$_3$ was treated with TMSPMA in xylene (TMSPMA/xylene: 90/10 v%) at 135?for 24 h.

To prepare the coating solution for PE separators, PVDF-HFP and TTT as a crosslinker were dissolved in acetone at room temperature. Surface-treated γ-Al$_2$O$_3$ was then put in this prepared solution, and uniformly dispersed by ball milling overnight. The weight ratio of the γ-Al$_2$O$_3$/PVDF-HFP/TTT mixtures was 90/10/0, 90/10/2, and 95/5/2.

Nanocomposite γ-Al$_2$O$_3$/PE separators were prepared by dip coating of PE separators in the above prepared solution and exposing them to humidified conditions (Relative Humidity 40%) followed by electron beam irradiation (Sohn et al., 2009), where coated-separators sealed in laminated aluminum /PE films were irradiated using a conventional 1 MeV electron beam accelerator (EB-tech Co. Ltd., Daejeon, Korea) at a radiation dose of 150 kGy, at a dose rate of 10 kGy/pass at room temperature.

2.3. Physical tests of *nanocomposite* γ-*Al$_2$O$_3$/PE separators*

The nanocomposite γ-Al$_2$O$_3$/PE separators were dried and sputter-coated with a thin gold film prior to SEM observation The morphologies of the prepared separators were observed using Scanning Electron Microscopy (SEM, Jeol JSM-6390).

The liquid electrolyte uptake was determined by soaking the obtained separators in a liquid electrolyte solution (1 M LiClO$_4$ in EC/DEC (1:1 v/v)) for 24 h. To remove the excess electrolyte adhering to their surfaces, the equilibrated samples were blotted using laboratory wipes and then weighed quickly. The liquid electrolyte uptake was determined from the difference in the weight of the dry samples and their swollen counterparts. All the procedures were carried out in an Ar-filled glove box (less than 5 ppm O$_2$ and H$_2$O).

The ionic conductivity of the separators soaked with the electrolyte solution at room temperature was determined using an AC impedance technique over the frequency range of 0.01–100 kHz using a Solatron SI 1260 frequency response analyzer combined with an SI 1287 electrochemical interface at a constant potential of 10 mV. The samples with area of A and thickness of L were sandwiched between two stainless steel blocking electrodes to measure their electrolyte resistance (R_b, Ω). The conductivity (σ, S/cm) was then calculated from Eq. (1).

$$\sigma = L/(R_b A) \tag{1}$$

The prepared separators were cut into 4 cm×4 cm pieces, and then subjected to a thermal shrinkage. Thermal shrinkages were determined by measuring the dimensional change after heating the samples in a forced convection oven at 150 °C for 1 h.

To investigate the linear sweep voltammetry, a virgin PE separator and the coated PE separators were soaked in a liquid electrolyte solution consisting of 1.0 M LiClO$_4$ in a 1:1 (v/v) ethylene carbonate (EC)/diethyl carbonate (DEC) mixture. Then, the soaked separators were sandwiched between lithium metal and stainless steel, and assembled into a tightly sealed test cell. The linear sweep voltammetry of the assembled test cells was measured in the range of 3–5.5 V at 5 mV/s.

A lithium-ion cell was assembled by sandwiching the prepared separator between a meso-phase carbon micro bead (MCMB) anode and a LiCoO$_2$ cathode after immersing them in the liquid electrolyte. The cathode was composed of 94 wt% of LiCoO$_4$ as a positive active material, 3 wt% of PVDF as a binder, and 3 wt% of super-P carbon as a conductive agent. The anode consisted of 93.5 wt% of MCMB as a negative material, 6 wt% of PVDF as a binder and 0.5 wt% of super-P carbon as a conductive agent. The cell was enclosed in a 2032-type coin cell. All assembly procedures of the cells were carried out in a dry box filled with argon gas. The discharge cycling tests of the lithium-ion polymer cells were conducted using Toyo battery test equipment (TOSCAT-3000U). The charging process was terminated at an end current of approximately 0.02 C rate (0.06 mA). The discharge current was fixed to a constant-current value with an end voltage of 3.0 V. The rest time was fixed to about 20 min between charge and discharge mode. All measurements were performed at room temperature.

3. Results and discussion

3.1. *Treatment of* γ-*Al$_2$O$_3$ particles with coupling agent*

It is known that the combination of γ-Al$_2$O$_3$ particles and polymers can improve the mechanical properties and thermal stability of polymers for use under extreme conditions (Kim et al., 2010; Jirawat et al., 2014; Giulio et al., 2010; Sohn et al., 2008).

A good adhesion and dispersion between two systems is one of the key factors determining the properties of the final products because the particles have a natural tendency to agglomerate due to the specific surface area and volume effects. One possible solution is to modify the surface of the particles by treating them with a proper coupling agent to