



Coating with macroporous polyarylate via a nonsolvent induced phase separation process for enhancement of polyethylene separator thermal stability

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ARTICLE INFO

Article history:

Received 7 December 2009
Received in revised form 14 January 2010
Accepted 6 February 2010
Available online 12 February 2010

Keywords:

Polyethylene separator
Nonsolvent induced phase separation
Macropores
Polyarylate
Coating
Thermal stability

ABSTRACT

Separator shutdown is a useful safety feature for preventing thermal runaway reactions in lithium ion batteries. Since after shutdown the cell temperature continues to increase before finally beginning to cool, the separator should maintain robust mechanical properties above the shutdown temperature to work as an insulator. To fabricate a separator that maintains its mechanical properties after shutdown, a polyethylene (PE) separator was coated with porous polyarylate (PAR) via a nonsolvent induced phase separation (NIPS) process. The formation of a porous coating layer on the PE separator and changes in morphology with the casting solution compositions were confirmed by electron microscopy. For the PE separator coated with macroporous PAR, the shutdown temperature (around 135 °C) was not changed, while the meltdown temperature increased to 188 °C with an acceptable reduction in air permeability.

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1. Introduction

Lithium ion batteries, which are widely used as power sources in portable electronic products, consist of an anode, cathode, porous film separator, and a rigid metal exterior [1–5]. Among these components, the separator, which is positioned between the anode and the cathode, offers protection against internal shorts and safe deactivation of the cell under overcharged conditions. Numerous studies have been performed to develop polymeric separators having high electrolyte permeability and good thermal, chemical, and electrochemical stabilities [6–18]. Separators for lithium ion batteries are mainly composed of microporous membranes fabricated from polyethylene (PE) or polypropylene (PP). When overcharged, a lithium ion battery starts to self-heat because of exothermic reactions that occur within the components of the cell. Separator shutdown is a useful safety feature for preventing runaway thermal reactions in lithium ion batteries. Shutdown occurs in the polyolefin separator as, around its melting temperature, the separator is turned into a non-porous insulated film due to pore collapse. Separators fabricated from PE and PP have shutdown temperatures at approximately 135 °C and 170 °C, respectively.

Since after shutdown, the cell temperature may continue to increase before finally beginning to cool, the cell may experience an internal short-circuit, creating a safety hazard when the mechan-

ical properties of the separator significantly deteriorate [16,17]. For this reason, the separator should maintain robust mechanical properties even above the shutdown temperature. Separators offering mechanical stability above the shutdown temperature of PE have been studied previously [13,17,18]. A separator having a porous PE layer sandwiched between two porous PP layers has been developed [17], with the PP layers providing mechanical stability above the shutdown temperature, while the PE layer offers a lower shutdown temperature. A PE separator coating with polymers synthesized from various ethylene glycol dimethacrylate monomers was previously examined in our laboratory [13]. Separators coated with polymers synthesized from diethylene glycol dimethacrylate (DEGDMA) had increased shutdown temperatures (approximately 140 °C) as well as meltdown temperatures (approximately 155 °C). However, this process was not feasible as a commercial process because it required a long reaction time (about 30 min) for the polymer coating layer to form on the separator from monomer.

In this study, the PE separator was coated with a macroporous polyarylate (PAR) film via a nonsolvent induced phase separation (NIPS) process [19–22] to reduce the processing time required for separator coating and to further enhance the meltdown temperature of the PE separator.

2. Materials and procedure

Polyethylene lithium battery separators made of high density polyethylene (grade: 320s) were provided by SK Energy Co. (Seoul, Korea). According to the supplier, the separators had a porosity

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of 46%, pore sizes in the range of 0.07–0.12 μm , and thicknesses of 20 μm . Polyarylate (PAR, $T_g = 200^\circ\text{C}$) purchased from Unitika (grade: U-100, Osaka, Japan) was used as the polymer to coat the PE separator surface. According to the supplier, this PAR is based on bisphenol-A with an equimolar mixture of isophthalic and terephthalic acids. Tetrahydrofuran (THF), used as solvent, and 2-butoxyethanol (or ethylene glycol butyl ether, EGBE), used as nonsolvent, were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA).

Separator coating with porous PAR was performed by a wet phase inversion process, i.e., a nonsolvent induced phase separation (NIPS) process. PAR was dried for at least 10 h at 140°C before being used in preparing the polymer solution. PAR was completely dissolved in THF by stirring for 10 h at 30°C and then the proper amounts of EGBE were mixed in to prepare the casting solutions. Note that ternary mixtures, which are formed from single-phase mixtures, were used as casting solutions in this study. The homogeneous polymer mixture was left without stirring until bubbles were completely removed. Casting with the resulting polymer solution was performed in a clean room at 30°C . The polymer solution was cast with a thickness of 100 μm onto a separator using a steel doctor blade. The casted separator was kept in a clean room at 30°C for a specific time to induce phase separation by evaporating the volatile solvent (THF). The resulting separator was immersed in a water bath for 24 h until the remaining nonsolvent and solvent were completely removed. The separator was then dried in a vacuum oven at 60°C for one day.

The phase boundary of PAR/THF/EGBE ternary mixtures was determined by observing solution turbidity with the naked eye. A series of THF solutions containing different amounts of PAR (PAR/THF = 3/97, 4/96, 5/95, 8/92, 10/90, and 13/87 by weight) were prepared in vials with a teflon-lined cap. Different amounts of EGBE were added to these solutions and mixed in an ultrasonic bath at 30°C for 1 h, and the resulting solutions were kept at 30°C for 24 h. Thereafter, if the solution was clear, it was judged to be thermodynamically stable and to have formed a homogeneous and single-phase mixture. If the solution was visually turbid, it was phase separated into two phases by liquid–liquid phase separation.

The morphologies of the separators were observed with a field emission scanning electron microscope (FE-SEM, model: JSM-6700F, JEOL, Japan). Changes in the air permeabilities of the coated separators were measured using the Gurley method (Technical Association of the Pulp and Paper Industry (TAPPI) T-460 method). A circular separator with an effective area of 6.45 cm^2 was placed in the testing equipment (model: G-B3C, Toyoseiki Co., Japan). The

time required for 100 cm^3 of air to pass through the separator under a pressure differential of 1.22 kPa was measured. Five specimens for each separator were tested, and their results were averaged. The shutdown temperature at which the pores on the PE separator completely disappeared from heating was measured by an annealing technique [13]. Separators mounted onto a cover glass were annealed on a hot plate (Linkam THMS 600) equipped with a temperature controller (Linkam, TMS 92) at a specific temperature around the melting temperature of PE ($120\text{--}140^\circ\text{C}$) for 5 min. The resulting separators were quenched to room temperature, and then changes in the morphology were observed by FE-SEM. By successively repeating the annealing process within the temperature range, the shutdown temperature of the separator was determined. The temperature at which meltdown started to occur was measured with a thermomechanical analyzer (TMA, model: Q400 TA Instruments, New Castle, USA). The displacement of the specimen (width \times length \times thickness = 6 mm \times 15 mm \times 20 mm) was monitored as a function of temperature at a scanning rate of $5^\circ\text{C}/\text{min}$ when a constant force of 0.015 N was applied. The temperature at which the specimen started to elongate was defined as the meltdown temperature. To confirm the meltdown behavior of the separator, changes in the specimen shape as a function of temperature were observed using a digital camera as the specimen was heated on a hot stage at a scanning rate of $5^\circ\text{C}/\text{min}$.

3. Results and discussion

3.1. Separator coating with macroporous PAR

Fig. 1 shows the phase diagram for the PAR/THF/EGBE ternary system. Only PAR/THF solutions containing ≤ 13 wt% of PAR were examined. Note that PAR did not completely dissolve in THF when >13 wt% of PAR was added to THF. The miscible region of the PAR/THF/EGBE system was very narrow, and its phase boundary was located close to the polymer–solvent axis. This suggests that miscible PAR/THF solutions readily undergo phase separation with the addition of small amounts of nonsolvent. It is known that a small nonsolvent tolerance is due to the relatively poor interactions between polymer and solvent and the high affinity between solvent and nonsolvent [21–24]. Nonsolvent tolerance gradually decreased as the polymer content in the ternary mixture increased. An increase of polymer content in solution always reduces the combinatorial entropy because the molecular weight of the polymer is much higher than that of the solvent (or nonsolvent), and

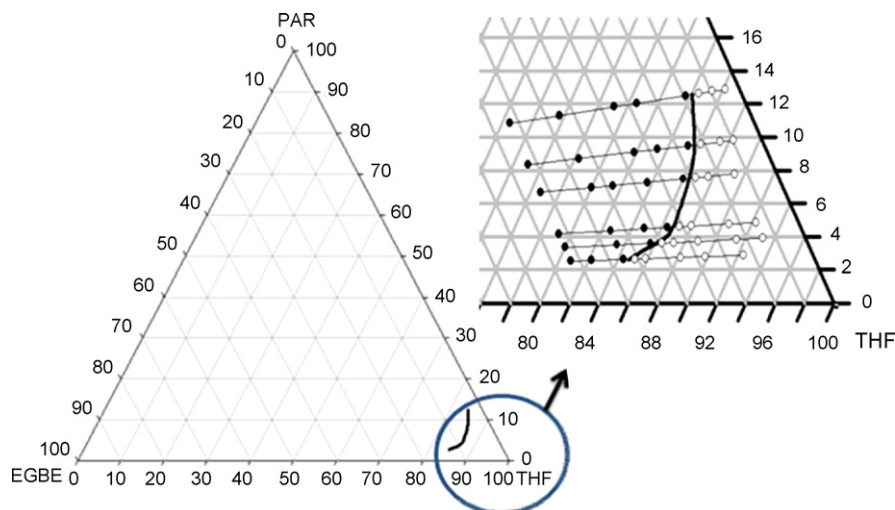


Fig. 1. Phase boundary of PAR/THF/EGBE ternary mixtures. Open circles represent miscible ternary mixtures while filled circles represent immiscible ternary mixtures.

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