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In-depth correlation of separator pore structure and electrochemical performance in lithium-ion batteries

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HIGHLIGHTS

- Well-defined polyethylene separators are fabricated with the same raw materials.
- Normalized Gurley number and ionic conductance can predict the cell performance.
- Correlation map on separators' physical and electrochemical properties is proposed.

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ABSTRACT

To establish an accurate correlation between a separator's pore structure and the electrochemical performance of a lithium-ion battery (LIB), we fabricate well defined polyethylene (PE) separators on the same production line while maintaining most processing variables, except for composition. Four PE separators having different thicknesses and porosities (16 μm/37%, 16 μm/40%, 16 μm/47%, 22 μm/47%, respectively) are physically and electrochemically evaluated in detail. Although thickness and porosity remain good parameters by which to represent the separators' characteristics, both the normalized Gurley number and ionic conductance are found to have much stronger relationships with the rate capability.

1. Introduction

Lithium-ion battery (LIB) separators, porous polymeric films tens-of-microns in thickness, are regarded one of the four major battery components, along with cathode and anode active materials and electrolyte. However, since they neither are electrochemically active nor exert a strong influence on the electrochemical performance of batteries, only limited investigation has been carried out in the battery field. Most previous studies have focused on fabricating new separators with different raw materials or manufacturing processes [1–4]. Several studies have correlated the physical properties of the separators with their electrochemical performance; however, these have been simple case studies that compared a variety of separators without in-depth control and analysis [5–9]. In this study, we explored this issue in greater detail by controllably fabricating separators with the same raw materials on the same production line. Under these conditions, most of the previously uncontrolled process variables were rigorously managed, and four polyethylene (PE) separators were obtained having thicknesses and porosities of 16 μm/37%, 16 μm/40%, 16 μm/47%, and 22 μm/47%, respectively. Their physical properties, microscopic morphologies, tensile stress, pore sizes and distributions, Gurley numbers, contact angles, liquid electrolyte

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uptakes, and thermal stabilities were precisely measured and analyzed. Then, their cycle performance and rate capabilities were evaluated in 2032-type coin cells. Finally, we proposed an in-depth correlation map between the physical properties and electrochemical performance of the separators.

2. Experimental

2.1. Separator fabrication

To fabricate well-defined PE separators having different porosities and thicknesses, we used the same raw materials and commercial production line, which was constructed by W-Scope Korea Co., Ltd. (Ochang province, Korea). The line is based on a wet process that includes an extrusion step to make a thick sheet, a two-axis elongation step, and a pore generation step via solvent extraction to control the pore structure and mechanical strength. The process is presented schematically in Fig. 1.

For the wet process, at least three-types of raw materials, a polymer, a pore generation material (i.e., a porogen), and an antioxidant, are needed to prepare the precursor mixture for extrusion. We used polyethylene (PE) (molecular weight (MW), 500,000 g mol^{-1}), a liquid-type paraffinic oil (1200 g mol^{-1}), and a phosphate ester. Based on the weight of the PE, the amounts of porogen material are controlled from 60% to 80% depending on the targeted porosity and thickness. The antioxidant was added into the mixture at levels of 6–10%. The weighed raw materials were combined and poured into a twin-screw extruder at 180–250 °C where they were mixed uniformly. The T-die extruded gel-state sheet was passed through two casting rolls at the temperatures range of 30–60 °C for cooling and to induce phase separation between PE polymer and porogen material. Then, the cooled, phase-separated sheet was drawn in two-axis directions, i.e., the machinery and transverse directions (MD and TD). As a result, the original sheet area could be enlarged by as much as 10 times, resulting in thicknesses of 16–22 μm. Finally, the stretched sheet was dipped in a solvent bath to remove the paraffinic oil, and then stored in an oven at 130 °C to remove the residual solvent and improve mechanical stress. Four types of separators were successfully fabricated in the commercial production line, and each separator was named according to its thickness and porosity: 16L: 16 μm/37%, 16M: 16 μm/40%, 16H: 16 μm/47%, 22H: 22 μm/47% (Table 1).

2.2. Physical analyses of the separators

The surface morphologies of the four separators were investigated by field emission scanning electron microscopy (FE-SEM, Hitachi, Japan). The sizes and distributions of the separator pores were quantitatively examined via a capillary flow porometer (PMI, USA). The permeability of the separators was assessed by determining the time required for 100 cm^3 air to pass through an area of 1 in^2 under a constant pressure (6.52 psig) using a densometer (4110 N, Thwing-Albert, USA). This procedure refers to the JIS (Japanese Industrial Standards)-P8117, and it is generally known to be Gurley number.

The wettability of separators toward liquid electrolyte was confirmed by measuring the contact angle of water with a contact angle analyzer (Phoenix-300Touch, SEO, Korea). Additionally, the uptake amount of liquid electrolyte by each separator was measured to calculate how much liquid electrolyte can be impregnated within the separator in more detail.

$$\text{Uptake amount (wt\%)} = \frac{W - W_0}{W_0} \times 100 \quad (1)$$

where W_0 and W indicate the separator weight before and after electrolyte absorption, respectively.

The tensile stress and strain were measured using a micro materials tester (Instron, USA). Each specimen was trimmed to a 15 mm width with a 150 mm length, and then pulled at a rate of 50 mm min^{-1}.

After cutting the separators into 3 cm × 3 cm squares, their thermal stabilities were evaluated by measuring their dimensional changes (Equation (2)) after 30 min in an oven at 140 °C. The following equation describes how to calculate this thermal shrinkage.

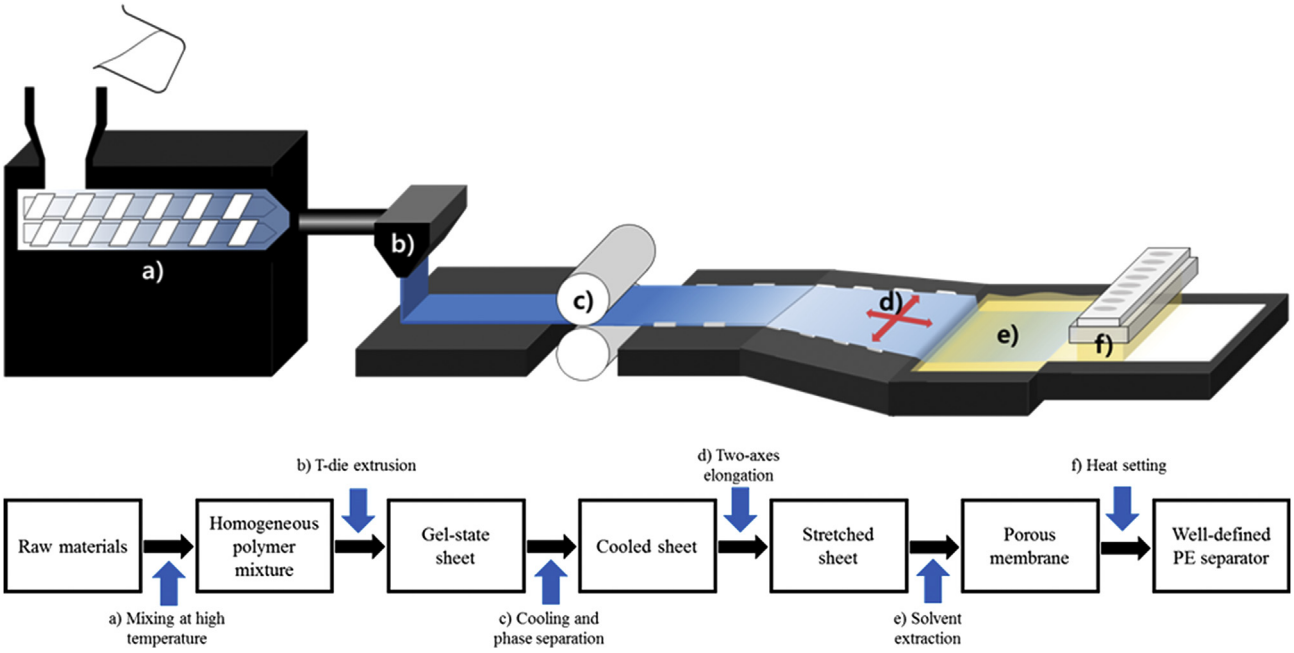

Fig. 1. Schematic of separator fabrication process.