



# Effect of microporous structure on thermal shrinkage and electrochemical performance of Al<sub>2</sub>O<sub>3</sub>/poly(vinylidene fluoride-hexafluoropropylene) composite separators for lithium-ion batteries

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## ABSTRACT

In a bid to develop a separator with improved thermal shrinkage that critically affects internal short-circuit failures of lithium-ion batteries, we demonstrate a new approach, which is based on introducing microporous composite coating layers onto both sides of a polyethylene (PE) separator. The composite coating layers consist of alumina (Al<sub>2</sub>O<sub>3</sub>) nanoparticles and polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP) gel polymer electrolytes. The microporous structure of the composite coating layers is considered a crucial factor governing the thermal shrinkage and electrochemical performance of the separators. The microporous structure is determined by controlling the phase inversion, specifically the solvent–nonsolvent miscibility, in the coating solutions. To quantitatively identify the effect of the solvent–nonsolvent miscibility, three different nonsolvents are chosen in the decreasing order of solubility parameter ( $\delta$ ) difference against the solvent (acetone,  $\delta = 20 \text{ MPa}^{1/2}$ ), which are respectively water ( $\delta = 48 \text{ MPa}^{1/2}$ ), butyl alcohol ( $\delta = 29 \text{ MPa}^{1/2}$ ), and isopropyl alcohol ( $\delta = 24 \text{ MPa}^{1/2}$ ). The microporous structure of the composite coating layers becomes more developed with the increase of not only the nonsolvent content but also the solubility parameter difference between acetone and nonsolvent. Based on this observation, we investigate the influence of the morphological variations on the thermal shrinkage and electrochemical performance of the composite separators.

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## 1. Introduction

As demands for higher energy-density lithium-ion batteries continue to grow, the accompanying safety concerns are issued as a critical challenge. A separator is considered a key component to prevent battery safety failures, because its primary function is to secure electrical isolation between a cathode and an anode of a battery [1–3]. In general, separators in lithium-ion batteries are made mostly of polyolefins, predominantly polyethylene (PE) or polypropylene (PP). These polyolefin-based separators are widespread and show many advantages, but they also have poor thermal shrinkage and mechanical strength. These drawbacks have led to serious concerns about maintaining the electrical isolation between the electrodes, particularly under conditions such as abnormal heating, or mechanical rupture. Recently, in a bid to overcome these drawbacks of polyolefin-based separators, many alternatives have been suggested, including self-standing inorganic separators [4,5], polyethylene terephthalate (PET) nonwoven-

inorganic composite separators [6], nonwoven fabrics consisting of para-phenylene terephthalamide (PPTA) fibers [7], and nanofiber-based separators prepared by electrospinning [8,9]. Among these approaches, the use of inorganic-based composite layers has received considerable attention because of their effectiveness in suppressing the thermal shrinkage and mechanical breakdown of separators.

In this study, as a new approach to significantly reduce the thermal shrinkage of a separator, we develop a new composite separator, which is based on applying the microporous composite coating layers onto both sides of a PE separator. The composite coating layers consist of alumina (Al<sub>2</sub>O<sub>3</sub>) nanoparticles and polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP) gel polymer electrolytes. To develop the microporous structure in the composite coating layers, we introduce phase inversion technique. Phase inversion is known to be an effective way to create porous structures in membranes, where a competitive mutual diffusion between solvent and nonsolvent occurs to yield porous structures [10,11]. A major objective of this study is to investigate the effect of phase inversion, specifically the solvent–nonsolvent miscibility, in the coating solutions, on the microporous structure evolution in the composite coating layers. To achieve this goal, three different non-

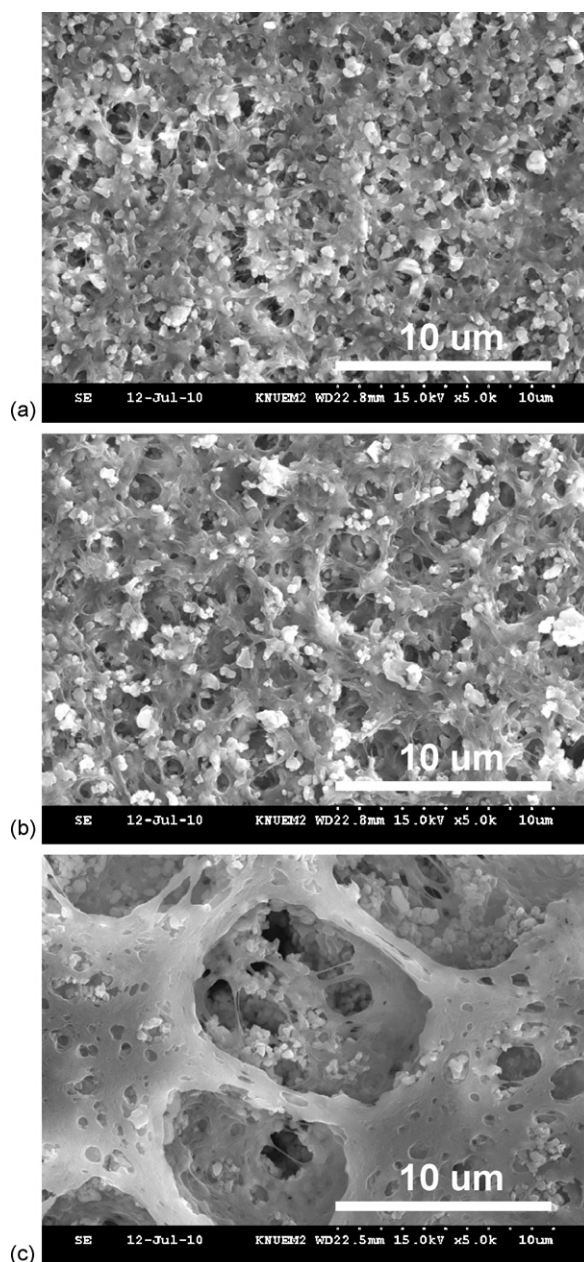
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solvents are chosen in the decreasing order of solubility parameter ( $\delta$ ) difference against the solvent (acetone,  $\delta = 20 \text{ MPa}^{1/2}$ ), which are respectively water ( $\delta = 48 \text{ MPa}^{1/2}$ ), butyl alcohol ( $\delta = 29 \text{ MPa}^{1/2}$ ), and isopropyl alcohol ( $\delta = 24 \text{ MPa}^{1/2}$ ) [12]. In addition, based on the understanding of the phase inversion, we quantitatively identify the influence of the morphological variations on the thermal shrinkage and electrochemical performance of the composite separators.

## 2. Experimental

The solutions for the composite coating layers were prepared by mixing  $\text{Al}_2\text{O}_3$  nanoparticles (average particle size = 480 nm) and PVdF-HFP (HFP content = 6 mol%) in acetone, where the composition ratio of  $\text{Al}_2\text{O}_3$ /PVdF-HFP was fixed at 50/50 (wt%/wt%). After first dissolving the PVdF-HFP in acetone, a fixed amount of  $\text{Al}_2\text{O}_3$  powders was added and the solution was further subjected to vigorous mixing via bead-milling for 2 h. To induce and control the phase inversion of the coating solutions, a specified amount of the nonsolvent (water, butyl alcohol, and isopropyl alcohol) was slowly added into the solutions. The nonsolvent contents in the solutions were varied from 2.83 wt% to 8.49 wt%. As a coating substrate, we chose a microporous PE separator (thickness = 20  $\mu\text{m}$ , Gurley value = 240 s 100  $\text{cc}^{-1}$ , porosity = 36%, thickness = 20  $\mu\text{m}$ , ExxonMobil Chemical). Using a dip-coating process, we applied the coating solution to both sides of the PE separator. The coated separator was then dried at room temperature to evaporate the acetone and further vacuum-dried at 50  $^\circ\text{C}$  for 4 h. The separator thickness was measured using a portable thickness gauge (Mitutoyo, Japan). As the solubility parameter difference ( $\Delta\delta$ ) between solvent (acetone) and nonsolvent increases, the separator thickness tends to increase, which reflects that the more porous structure is developed in the composite separator. For example, at a fixed nonsolvent content of 8.49 wt%, the thickness of composite separator was measured to be  $\sim 30 \mu\text{m}$  (acetone–isopropyl alcohol),  $\sim 32 \mu\text{m}$  (acetone–butyl alcohol), and  $\sim 43 \mu\text{m}$  (acetone–water).

The microporous structure, air permeability, porosity and thermal shrinkage of separators are key characteristics to be carefully monitored. The air permeability was examined with a Gurley densometer (4110N, Gurley) by measuring the time necessary for air to pass through a determined volume under a given pressure. The air permeability represented by a Gurley value (s 100  $\text{cc}^{-1}$ ) is considered a useful parameter for predicting ionic conductivity of a separator, where a low Gurley value indicates high air permeability [1–5]. The porosity ( $= (\rho_c - \rho_e) / \rho_c$ ) of composite coating layers was obtained by measuring their density, where  $\rho_c$  is the calculated density for a dense coating layer (assumed to be without pores) and  $\rho_e$  is the experimental density for a porous coating layer. The surface morphology of composite coating layers was investigated using field emission scanning electron microscopy (FE-SEM, S-4300, Hitachi). The thermal shrinkage of separators was determined by measuring the dimensional change (area-based) after they were subjected to heat treatment at various temperatures for 0.5 h. To measure the electrochemical performance, a liquid electrolyte of 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1, v/v, Technosemi Chem) was employed. For measurement of the ionic conductivity of the composite separators as well as the pristine PE separator, the separators were first immersed in the liquid electrolyte and then sandwiched between the stainless-steel (SS) electrodes. The ionic conductivity of the separators was obtained by measuring the bulk resistance obtained from AC impedance analysis using a VSP classic (Bio-Logic) over a frequency range of 1 Hz to 10<sup>6</sup> Hz. A lithium half-cell (2032-type coin cell) was assembled by sandwiching the separator between a lithium-metal anode and a  $\text{LiCoO}_2$  cathode and then activated



**Fig. 1.** FE-SEM photographs of  $\text{Al}_2\text{O}_3$ /PVdF-HFP (=50/50 wt%/wt%) composite coating layers as a function of solubility parameter difference ( $\Delta\delta$ ) between solvent (acetone) and nonsolvent in coating solutions: (a) acetone–isopropyl alcohol system ( $\Delta\delta = 4 \text{ MPa}^{1/2}$ ), (b) acetone–butyl alcohol system ( $\Delta\delta = 9 \text{ MPa}^{1/2}$ ), and (c) acetone–water system ( $\Delta\delta = 28 \text{ MPa}^{1/2}$ ), where a nonsolvent content is fixed at 8.49%.

by filling the liquid electrolyte. All assembly of cells was carried out in an argon-filled glove box. The discharge C-rate capability of cells was examined using a battery test equipment (PNE Solution), where discharge C-rates were varied from 0.2 C (=0.68  $\text{mA cm}^{-2}$ ) to 2.0 C (=6.81  $\text{mA cm}^{-2}$ ) at a constant charge C-rate of 0.2 C under a voltage range between 3.0 V and 4.3 V.

## 3. Results and discussion

We investigate the effect of solvent–nonsolvent miscibility in the coating solutions on the microporous structure evolution of the composite coating layers as a function of the solubility parameter difference ( $\Delta\delta$ ) between solvent (acetone) and nonsolvent. Fig. 1 shows that as the solubility parameter difference increases from

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