



Expanded polytetrafluoroethylene reinforced polyvinylidene fluoride–hexafluoropropylene separator with high thermal stability for lithium-ion batteries



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HIGHLIGHTS

- Porous polytetrafluoroethylene stabled separator for Li-ion battery.
- Highly thermal stability and low thermal shrinkage.
- Excellent capacities at high rate discharge.

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ABSTRACT

PVDF–HFP/ePTFE composite separator with high thermal stability and low thermal shrinkage characteristic has been developed. The PVDF–HFP acts to absorb the electrolyte and shutdown at elevated temperature. The thermally stable ePTFE matrix is adopted to improve the mechanical strength and sustain the insulation after the shutdown. This novel separator presents good ion conductivity (up to 1.29 mS cm^{-1}) and has a low thermal shrinkage of 8.8% at $162 \text{ }^\circ\text{C}$. The composite separator shutdown at $162 \text{ }^\circ\text{C}$ and keep its integrity before $329 \text{ }^\circ\text{C}$. Cells based on the composite separator show excellent capacities at high rate discharge and stable cycling performance.

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1. Introduction

The application of lithium-ion batteries has been expanding from electronic devices to power tools and electric vehicles, due to their high capacity and long cycle life. Intensive research has been conducted to improve the performance of lithium batteries, such as energy densities and abuse tolerance of batteries. Among them, safety presents a critical challenge and numerous methods have been developed to suppress the failure [1–3].

The separator in a battery plays an important role to retain electrolyte, prevent shortage between the two electrodes while maintaining high ion permeation, and to perform safe deactivation of the cell under overcharge, abnormal heating or mechanical rupture conditions [4]. Currently widely used separators in lithium-

ion batteries are most commonly fabricated by polyolefins such as polypropylene (PP) and polyethylene (PE), which will shrink or melt at elevated temperatures and cause an internal short-circuit, as well as poor in wettability. In order to overcome these limitations, various approaches have been addressed. Such as impregnation of gel polymer electrolytes into nonwovens [5–8], coating of gel polymer or ceramic powders to polyolefin separators [9–15], and other fabrication techniques [16–20]. Although improvement in thermal shrinkage and wettability has been observed, further improvement is still desired for applications which require more safety assurance. For example, when the internal temperature of the power battery excessively increases, the porous separator should partially melt to clog its micropores, which increases the impedance of the battery and consequently prevents the further reaction. Moreover, this shutdown state should be continuously maintained before the cooling down of the battery, and a wide shutdown window is necessary.

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In this study, a composite separator comprising a microporous polyvinylidene fluoride–hexafluoropropylene (PVDF–HFP) layer and an expanded polytetrafluoroethylene (ePTFE) matrix support was developed. The PVDF–HFP serves to absorb the liquid electrolyte and shutdown at elevated temperature. The ePTFE matrix acts to reinforce the mechanical strength and keep the integrity to prevent short-circuit after the shutdown of PVDF–HFP layer. The porosity of composite separator is determined by controlling the content of pore-forming agent (PEG). Mechanical, thermal and electrochemical properties, as well as the morphology of the composite separators have been studied systematically. The contents of PEG have also been changed to understand the effects of these variables on the properties of prepared separators.

2. Experimental

2.1. Preparation of composite separators

PVDF–HFP with an average molecular weight of 450,000 (pellets, Aldrich, USA), polyethylene glycol (PEG) with an average molecular weight of 20,000 (Sinopharm Chemical Reagent Co., Ltd.), other solvents were reagent grade and used as received.

To prepare the casting solution, 8 g of PVDF–HFP was dissolved in a 60 ml mixture of high boiling-point solvent (DMF) and volatile solvent (acetone) with the volume ratio of 1–2. Due to the low surface energy of ePTFE matrix, the proportion of the high boiling-point solvent is low enough to allow the wetting of ePTFE and high enough to allow phase separation during evaporation [21]. In the PVDF–HFP solution, various amounts of PEG were added under vigorous stirring at 60 °C for 12 h (the weight ratios of PEG/PVDF–HFP were 30%, 50%, 70%, 90% and 110%, respectively).

Porous ePTFE membranes (porosity = 85%, thickness = 6 μm, pore size = 1–2 μm, Dagong Co., Shanghai, China) were used as the matrix of the composite separator. The matrix membrane was first mounted on 10 cm × 10 cm plastic frame and dried in a vacuum oven at 60 °C for 1 h to remove water. The frame was laid in a Petri dish. The casting solution was poured on the ePTFE matrix. The Petri dish was sealed at 30 °C for 30 min for impregnation. Then the impregnated membrane was dried at 100 °C in a vacuum oven for 6 h to remove the organic solvents. The composite separator was immersed in a pool of deionized water for 12 h to remove the PEG from PVDF–HFP and generate porous structure. The separator was then dried at ambient temperature.

2.2. Characterization of the composite separators

2.2.1. Morphology of composite separators

The morphologies of separators were examined using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi). The tensile strength was determined by using a Tensile Tester (Hualong WDW-0.5). The electrolyte uptake and porosity are measured by immersing the membrane into n-butanol and liquid electrolyte separately for 30 min and calculating with the following equation:

$$\text{Porosity}(\%) = 100 \times \frac{M_x/\rho_x}{M_x/\rho_x + M_y/\rho_y}$$

$$\text{Electrolyte uptake}(\%) = 100 \times \frac{W_i - W_o}{W_o}$$

where M_x and M_y are the weight of n-butanol absorbed and the dried composite separator, respectively. ρ_x and ρ_y are the density of

n-butanol and the dried composite separator, respectively. The density of composite separator was determined by measuring the volume and the weight. W_i was the weight of the wet separator soaked with electrolyte and W_o was the weight of dry separator. The extra solution (n-butanol or electrolyte) at the surface of the separator was absorbed with a filter paper before measuring weight.

2.2.2. Thermo shrinkage and shutdown property

DSC and TGA scans were performed with a simultaneous TG-DSC system (STA 449F3, NETZSCH) at the rate of 5 °C min⁻¹ under nitrogen purge from 30 °C to 350 °C. TMA tests were performed on a TMA analyzer (TMA202, NETZSCH) under N₂ atmosphere and the temperature was increased 5 °C min⁻¹ from 30 °C to 200 °C, with a constant external tensile force of 0.02 N. A heat plate is used to present the thermo shrinkage instantaneously.

To prepare the cell for high temperature test, the cell was assembled by sandwiching the separator between a MCMB (Mesophase Carbon Micro Beads) anode and a LiFePO₄ cathode and then activated by filling liquid electrolyte. Then it was sealed in a CR2032 shell with the pressure of 50 kg cm⁻² by using a sealing machine (MSK-110, MTI Corp.). All the cells were first charged to 75% state of charge (SOC) using battery test equipment (CT2001A, LAND Electronics) and were left at OCV condition for 24 h, and then was heated in a heating mantle from room temperature to around 200 °C at which the OCV drops to zero. The temperature is increased at the rate of 10 °C min⁻¹ and was measured with a thermometer (YC-727UD, Tenmars) by attaching the thermocouple to the cell surface. The OCV was measured using an electrochemical workstation (CHI604D, CH Instruments).

2.2.3. Electrochemical measurements

The composite separators were sufficiently soaked in a liquid electrolyte in an Ar-filled glove box. The electrolyte contained 1 M LiPF₆ in ethylene carbonate (EC)–diethyl carbonate (DEC)–ethyl methyl carbonate (EMC) (v/v/v = 1/1/1, Samsung Cheil Industries). The soaked separators were sandwiched between two stainless steel electrodes and assembled into a tightly sealed test cell. The ionic conductivity at various temperatures was determined by an AC impedance analysis using an electrochemical workstation (CHI604D, CH Instruments) over the frequency range of 10 Hz–10⁵ Hz and under an AC voltage of 5 mV. It was calculated from the following equation:

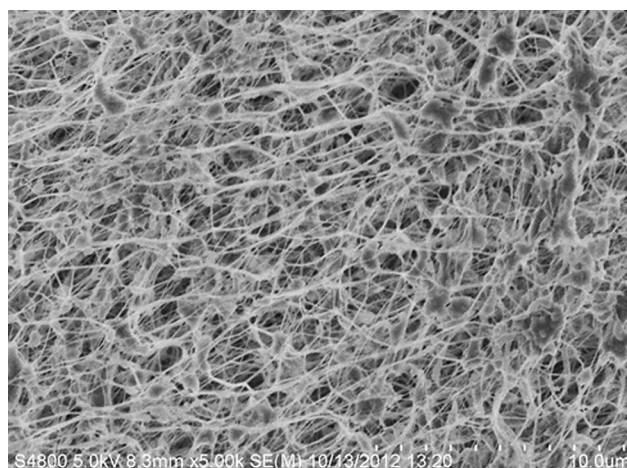


Fig. 1. FE-SEM photographs (surface) of pristine ePTFE matrix.

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