

Effect of silica nanoparticles/poly(vinylidene fluoride-hexafluoropropylene) coated layers on the performance of polypropylene separator for lithium-ion batteries

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[Manuscript received February 17, 2014; revised April 9, 2014]

Abstract

In an effort to reduce thermal shrinkage and improve electrochemical performance of porous polypropylene (PP) separators for lithium-ion batteries, a new composite separator is developed by introducing ceramic coated layers on both sides of PP separator through a dip-coating process. The coated layers are comprised of heat-resistant and hydrophilic silica nanoparticles and polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) binders. Highly porous honeycomb structure is formed and the thickness of the layer is only about 700 nm. In comparison to the pristine PP separator, the composite separator shows significant reduction in thermal shrinkage and improvement in liquid electrolyte uptake and ionic conduction, which play an important role in improving cell performance such as discharge capacity, C-rate capability, cycle performance and coulombic efficiency.

Key words

composite separator; silica nanoparticles; dip-coating; thermal shrinkage; cell performance

1. Introduction

A separator is one of the indispensable components in a lithium-ion battery (LIB). It plays two roles in a cell: isolate the cathode and anode to prevent internal short circuits and provide a path for ionic conduction through the liquid electrolyte which fills in its porous structure [1–5]. Currently, the most extensively used separators are made of polyolefin through multiple stretching processes, such as polyethylene (PE) and polypropylene (PP). Although these separators offer many advantages, their unsatisfactory thermal stability has raised serious concerns regarding the shrinkage at elevated temperatures which leads to the ignition or explosion of cells. Furthermore, since they are incompatible with liquid electrolyte, polyolefin separators have low liquid electrolyte uptake which may affect ionic conductivity [6–9].

Among the variety of approaches to overcome these drawbacks, the introduction of composite layers has attracted substantial attention, due to their superiority in preventing thermal shrinkage and enhancing electrolyte uptake [10,11]. It can be achieved by binding inorganic nanoparticles on both sides of pristine separators with polymeric binders. Due to their

excellent thermal stability and wettability of inorganic particles with liquid electrolyte, composite separators significantly improve thermal stability and electrochemical performance [12–14]. However, in order to disperse nanoparticles evenly in the solvents, ultrasonication dispersion and ball milling have to be used which result in an added processing. Furthermore, the thickness of the coated layer is more than 4 micrometers [15–17], which is too thick to decrease electrical resistance and take up limited space inside the battery, which lowers energy and power densities of cells and adversely affects battery performance [18].

In this paper, a composite separator is prepared by binding SiO₂ nanoparticles on the surface of PP with polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) binder. The dispersed SiO₂ nanoparticles are obtained via simple agitation and the thickness of the coated layer is only about 700 nm. The influence of coated layer on the separator surface and cross-section morphology, thermal shrinkage, electrolyte uptake, ionic conductivity and cell performances such as discharge capacity, discharge C-rate capability, cyclability and coulombic efficiency is investigated, and compared with those obtained with the pristine PP separator.

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This work was supported by the Tsinghua University Initiative Scientific Research Program (Grant No. 2012THZ08129).

2. Experimental

2.1. Preparation of separators

0.4 g PVDF-HFP (Kynar Flex 2801, 12 wt% HFP) was dissolved in 60 mL mixed solvent. Then SiO₂ nanoparticles of 1.2 g with an average particle size of 50 nm, provided by Hangzhou Wanjing New Material Co., Ltd, China were added into the solution under vigorous stirring for 10 min. Subsequently, the solution containing SiO₂ nanoparticles was further dispersed by a continuous agitation for 5 h.

As a coated substrate, a microporous PP separator (Celgard 2400) was chosen. The solution with dispersive SiO₂ nanoparticles was coated on both sides of the PP separator by a dip-coating process. The separators were then dried at room temperature to evaporate solvents.

2.2. Characterization of separators

The surface and cross-section morphology of coated layers were investigated by scanning electron microscope (SEM, JSF7401). The thermal shrinkage of the separators was determined by measuring the dimensional change after being subjected to heat treatment at various temperatures for 0.5 h. The electrolyte uptake was measured by immersing the separators in 1/1 (v/v) mixture of ethylene carbonate (EC) and diethylene carbonate (DEC), and calculated using the following formula [19]:

$$\text{Membrane liquid uptake} = [(w_t - w_0) / w_0] \times 100\%$$

where, w_0 is the weight of the dry separator and w_t is the weight of the separator after fully swelling.

2.3. Electrochemical measurement

The liquid electrolyte was prepared by dissolving 1 mol/L LiPF₆ in mixed solvents (DEC/EC = 1/1 in volume). The ionic conductivity of the separators was measured by AC impedance analysis [20] over a frequency range between 1 Hz to 10⁵ Hz.

Lithium half-cells (2032-type coin) were assembled by sandwiching the separator between lithium-metal anode and

LiCoO₂ cathode, and then activated by introducing the liquid electrolyte. The cathode consists of 85 wt% LiCoO₂ (Shanshan Co. Ltd), 5 wt% carbon black, 5 wt% conductive graphite and 5 wt% binder. Cells were charged up to 4.2 V and discharged to 2.75 V at various C-rates. The cell assembly was carried out in an argon filled glove box and all cells were conducted using Land Battery Test System (Wuhan Land Electronic Co. Ltd, China).

3. Results and discussion

3.1. Morphologies of separators

Surface images of the pristine and coated separator are shown in Figure 1(a) and 1(b). In contrast to uncoated PP separator (Figure 1a), Figure 1(b) shows that a SiO₂/PVDF-HFP coated layer is successfully formed on the PP separator surface. SiO₂ nanoparticles are close-packed and interconnected by PVDF-HFP binder. These coated layers are expected to prevent the separators from being thermally shrunk, owing to the existence of heat-resistant SiO₂ nanoparticles. It is noteworthy that well-connected interstitial voids which show a honeycomb structure are formed between SiO₂ nanoparticles. These unique interstitial voids will be filled with liquid electrolyte and may provide a facile pathway for ion movement, contributing to high liquid electrolyte uptake and ionic conduction. In order to provide a visual understanding of the coated thickness, cross-section image of the coated separator is shown in Figure 1(c). The thickness of the coated layer is only 700 nm and the cross-section also has a highly porous structure as the surface. Therefore, the composite separator has little effect on energy and power densities of the cells due to thinner thickness and highly porous structure of the coated layers.

3.2. Thermal stability

As the essential role of the separator is to isolate the anode and cathode to prevent internal short circuits, the separator should be stable in the cell. As the starting melting point of PP separator is about 168 °C and it is prepared by multiple

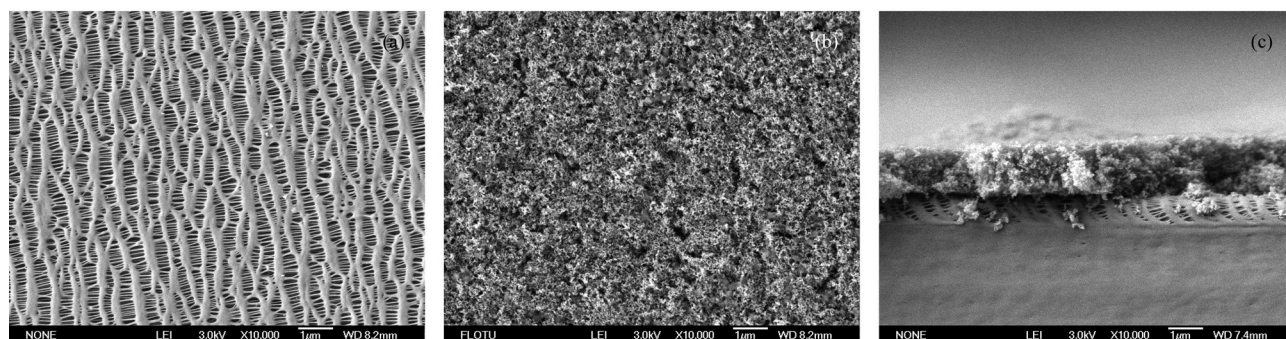


Figure 1. SEM images of (a) pristine PP separator, (b) SiO₂/PVDF-HFP coated PP separator and (c) cross-section image of SiO₂/PVDF-HFP coated layer

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