



A paper-supported inorganic composite separator for high-safety lithium-ion batteries



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ABSTRACT

A paper-supported inorganic composite (PIC) separator is prepared by spraying Al_2O_3 particles onto both surfaces of a commercial paper substrate. The as-prepared PIC separator shows excellent thermal stability without any shrinkage at 130 °C for 30 min, superior wettability towards the electrolyte, with a contact angle of 0°, and high ionic conductivity compared with that of the conventional polyethylene (PE) separator. The graphite|LiCoO₂ full-cells with the PIC separator exhibit good cycling and rate performance. In the nail penetration tests, the pouch cell assembled with the PIC separator shows high safety characteristics. Given the advantages of the PIC separator, it is a good potential replacement for the polyolefin separators used in high-safety lithium-ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) have been the leading power sources in consumer electronics and electric vehicles (EVs) and are receiving increasing attention for use in large-scale energy storage systems in smart grids because of their advantages of high energy density and long lifetime [1–4]. Although LIB technologies have recently experienced rapid developments, significant improvements in energy density and safety characteristics are still desired. With the increasing energy density of batteries and the development of large-sized LIBs, the safety characteristics of LIBs are becoming increasingly important. As the organic components, the nonaqueous electrolyte and the separator strongly influence the safety characteristics of batteries. When thermal runaway is triggered, the flammable properties of the nonaqueous electrolyte might cause a fire or even an explosion [5]. A high-safety LIB should fundamentally avoid thermal runaway even under various abuse conditions such as a short circuit, nail penetration, high temperatures or overcharging.

Generally, the separator that physically separates the positive and negative electrodes is critical to battery safety. The dominant separators used in the state-of-the-art LIBs are polyolefin (polyethylene (PE), polypropylene (PP) or their composites) microporous membranes.

These organic membranes with low melting points (135 °C for PE, 165 °C for PP) easily suffer from severe dimensional shrinkage at elevated temperatures, and the resulting internal short circuit can trigger the thermal runaway of LIBs [6,7]. Therefore, alternative separators with superior thermal stability must be developed to meet the requirements for high-safety or large-scale batteries.

Many efforts have been made to overcome the thermal shrinkage of polyolefin separators. In our previous reports [8,9], we prepared pure inorganic (Al_2O_3 and SiO_2) separators without binders; they exhibited superior thermal stability because they were prepared via high-temperature treatments. Nevertheless, these pure inorganic separators are fragile; they can therefore be used only in limited applications. Recently, we prepared a thin and flexible inorganic composite separator with ~ 94% Al_2O_3 and ~ 6% styrene-butadiene rubber (SBR) binder [10]. This composite separator exhibited thermal stability comparable to that of pure inorganic separators. Introduction of the binder made the separator flexible, but its mechanical properties are still poor.

To obtain inorganic composite separators with good mechanical strength, ceramic-coated separators have been widely investigated [11–20]. Two basic types of ceramic-coated separators have been developed. One type entails coating inorganic (ceramic) powders onto commonly used polyolefin separators to alleviate their thermal

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shrinkage [12–15,18]. This type of inorganic composite separator inherited the shutdown function of polyolefin separators as well as their high cost. Moreover, the polyolefin component in the composite separator still undergoes large shrinkage ($\sim 20\%$ at $> 140^\circ\text{C}$) at some elevated temperature [14], which is sufficient to induce safety concerns for the batteries. The other type of inorganic composite separator is coating of inorganic (ceramic) powders onto non-woven mats as the substrate [17]. Nevertheless, traditional non-woven mats with large-fibre diameters and pore sizes are suitable as the separators for lead-acid batteries but not for LIBs [21]. Even though the highly porous non-woven mats with reduced fibre diameters prepared by electrospinning are attractive as LIB separators, their cost poses a substantial challenge for their wide application [22]. Therefore, developing an alternative and low-cost substrate for inorganic composite separators is an important objective.

Recently, paper-based separators have attracted interest because of their low production costs and good mechanical properties [23–25]. Because of the existence of some large pores, single-layer commercial paper, e.g., rice paper [23], is inappropriate for use as a separator for LIBs. Nevertheless, most tissue paper is low-cost and facile, and its large porous structure has negligible resistance to electrolyte permeation and Li^+ -ion transport. Therefore, tissue paper should be a good substrate for inorganic composite separators.

In this study, we use single-layer commercial paper as the substrate to fabricate a paper-supported inorganic composite (PIC) separator for high-safety LIBs. As illustrated in Fig. 1, the inorganic particles (Al_2O_3) and a small amount of polymer binder (styrene-butadiene rubber, denoted as SBR) is dispersed into water, and the resulting suspension is subsequently sprayed onto the paper using compressed air. This coating procedure involving spraying of an aqueous suspension is environmentally friendly and highly effective for production. Additionally, the structure and thickness of the coating layer can be adjusted more easily with this spraying method than with the commonly used casting method. The PIC separator inherits the advantages of the paper substrate, i.e., low cost, high porosity, good flexibility and appropriate strength. Moreover, the PIC separator exhibits excellent thermal stability and wettability towards nonaqueous electrolytes; consequently, batteries fabricated using the PIC separator show a higher rate capability and better safety characteristics than batteries fabricated using a commercial PE separator.

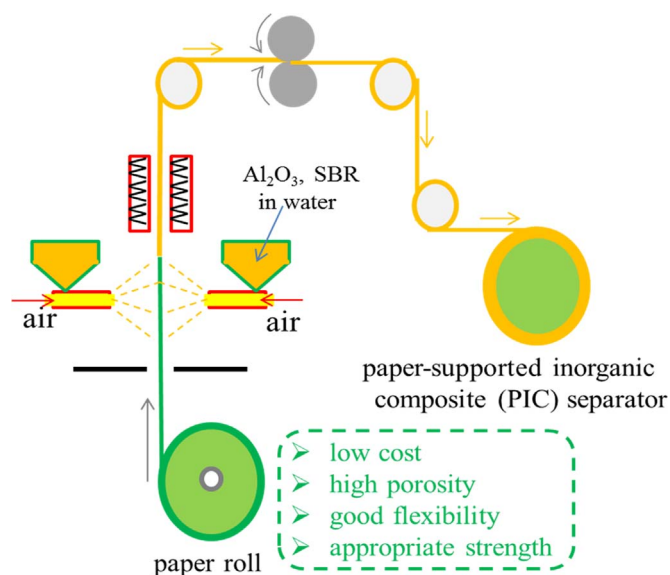


Fig. 1. Schematic of the PIC separator preparation process.

2. Experimental

2.1. Preparation of the PIC separator

The PIC separator was prepared by a spray-coating method. First, neutral activated alumina (Al_2O_3) (300 mesh, Sinopharm Chemical Reagent Co., Ltd.) and Al_2O_3 ultrathin particles (100–300 nm, Xianzheng Co., Ltd.) were mixed at a mass ratio of 1:3. The mixed Al_2O_3 particles and SBR (Jingbang Power Source Co., Ltd.) with polyethylene glycol (PEG, M.W. = 200, Sinopharm Chemical Reagent Co., Ltd.) were then mixed thoroughly in deionized water to form a viscous slurry at room temperature. The weight ratio of Al_2O_3 , SBR and PEG was 94:6:1. The components are based on our previous paper [10]. The suspension was then sprayed onto tissue paper (Gold Hongye Paper Co., Ltd.) using an airbrush. The distance between the paper and the airbrush was 40 cm. After drying at 55°C , the as-prepared membrane was pressed by double rollers; the thus-obtained PIC separator was cut into discs ($\phi 16$ mm) for testing.

2.2. Battery assembly

Cell performance of the PIC separator was evaluated in CR2032-type coin cells with a LiCoO_2 positive electrode and a graphite negative electrode. To make a positive-electrode laminate, 84 wt% LiCoO_2 (Amperex Technology Limited), 8 wt% carbon conductive additive (Super-P, TIMCAL) and 8 wt% polyvinylidene fluoride (PVDF, Solef 5130, Solvay) were dispersed in *N*-methyl-2-pyrrolidinone (NMP, Sinopharm Chemical Reagent Co., Ltd.) to form a positive-electrode slurry, which was then spread onto an aluminium foil current collector. To make a negative-electrode laminate, 90 wt% commercial graphite (FT-1), 3 wt% Super-P and 7 wt% PVDF were dispersed in NMP to form a negative-electrode slurry, which was then spread onto a copper foil current collector. After vacuum drying at 80°C for 4 h, both the positive and negative laminates were punched into discs ($\phi 14$ mm) for assembling the coin cells. The mass loadings of the positive and negative electrodes were controlled at ~ 4.38 mg cm^{-2} and ~ 2.06 mg cm^{-2} , respectively. The specific capacity of the LiCoO_2 /graphite full-cell was calculated on the basis of the mass of LiCoO_2 . The electrolyte was 1 mol L^{-1} LiPF_6 /ethylene carbonate (EC) + dimethyl carbonate (DMC) (1:1, w/w). The LiCoO_2 /graphite cells were assembled in an argon-filled glove box (MBraun).

Pouch cells were used to evaluate the safety characteristics of the PIC separator. The method used to fabricate the electrodes for pouch cells was similar to the previously described method except that both sides of the aluminium or copper current collectors were cast using the positive- or negative-electrode slurry, respectively. The capacity of the pouch cells was designed to be 350 mA h. For comparison, a commercial PE separator was also incorporated into both coin cells and pouch cells.

2.3. Characterization

The morphologies of the PIC separators were observed by field-emission scanning electron microscopy (FESEM, Hitachi SU8020). The thermal stabilities of the separators were determined by thermal shrinkage tests at 130°C for 30 min. The porosities of the separators were determined using 1-butanol uptake tests. In an uptake test, the porosity of the tested separator was calculated using the following Eq. (1) [26,27]:

$$\text{Porosity}(\%) = \frac{W_w - W_d}{\rho_b V} \times 100\% \quad (1)$$

where W_w and W_d are the weights of the wet and dry separator, respectively; ρ_b is the density of 1-butanol, and V is the geometric volume of the separator. The electrolyte wettability of the separators was determined by two methods: the electrolyte immersion height test and the

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