



Polypropylene/hydrophobic-silica-aerogel-composite separator induced enhanced safety and low polarization for lithium-ion batteries



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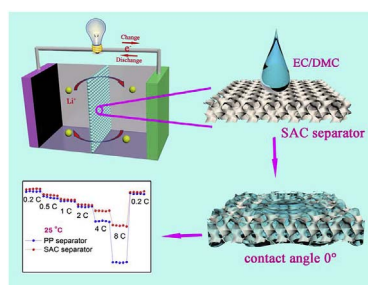
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HIGHLIGHTS

- SAC separator is fabricated by combining hydrophobic silica aerogel and PP separator.
- The SAC separator has excellent wettability to several different electrolytes.
- The SAC separator can improve the power performance Li-ion batteries.
- The SAC separator shows negotiable abscission after folding 200 times.
- The obtained SAC separator enhances the safety of Li-ion batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

Separator as an important part of lithium-ion batteries, allowing the ion to transfer and preventing the direct contact of anode with cathode, determines the safety of the batteries. In this work, a kind of polypropylene/hydrophobic silica-aerogel-composite (SAC) separator is fabricated through combining hydrophobic silica aerogel and polypropylene (PP) separator. The rationally designed SAC effectively increases the thermal stability of the separator with slightly growing weight (the area retention rate is 30% higher than that of the PP separator after being heated for 30 min at 160 °C). In addition, the hydrophobic silica aerogel layer in SAC significantly improves the wettability of PP separator to electrolyte owing to the introduced hydrophobic functional groups of $-\text{Si}(\text{CH}_3)_3$ and porous structure, and the contact angles of SAC separator to several common organic electrolytes (EC/DMC, DMC/DOL, Diglyme) are close to 0°. Electrochemical tests show that the prepared SAC separator can decrease the polarization of Li-ion batteries and leads to improved power performance and cycle stability. And the SAC separator is firm with neglectable abscission after folding 200 times. This work provides a new way to improve the safety and simultaneously reduce the polarization of the batteries, implying promising application potential in power batteries.

1. Introduction

Recently, environmental-friendly energy storage devices with high energy density and long cycle life have attracted great attention to meet the ever-increasing energy storage needs for various technological

applications, including electronic products, electric tools, hybrid and electric vehicles, and large-scale renewable energy storage [1,2]. Therefore, a number of researchers have been focusing on the investigation of electrochemical active materials with high capacity, voltage platform and long cycle stability [3,4]. As a crucial component

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of energy storage devices, the separator has a discordant development. Apart from preventing contact between two electrodes, separators strongly affect the cycle stability, safety and rate performance of batteries [5,6]. Polyolefin, as a successfully commercialized separator for LIBs, have numerous advantages, such as low cost, good flexibility, relatively high mechanical strength, and inherent thermal shutdown property [7]. (When the internal temperature of the battery reaches the melting point of polyolefin separator, the pore of polyolefin separator will automatically shut down and cut off the ion transmission path, so as to terminate the battery reactions and avoid further temperature rising). However, the low melting temperature of polyolefin separator leads to a potential security risk of batteries [8–10]. Besides, poor wettability and low electrolyte retention of polyolefin separator hinder the ion transport efficiency, enlarge the internal resistance and electrode polarization, and decrease the actual specific energy of the batteries [11].

In order to overcome these obstacles, multiple approaches have been developed. The first one is the coating or dipping method, these composite separators were fabricated by coating inorganic or organic materials on polyolefin separator, such as Al_2O_3 [12], SiO_2 [13–15], TiO_2 [16], Tannic acid [17], Poly (ethylene oxide) [18], and Poly-methyl methacrylate [19] etc. These composite separators have promoted the thermal stability and wettability to a certain extent, while some other disadvantages still exist. For example, traditional inorganic coating layers without three-dimensional structure have higher density, causing the low energy density of batteries. And the ability of the organic coating layers to promote the thermal stability of the separator is relatively poor. The second type is nonwoven separators, which have been reported to show excellent wettability [20–23] and good heat resistance [24,25], yet they are difficult to achieve large-scale commercial application. Nonwovens also do not have the thermal shutdown characteristic. In addition, dipping growth method is also known to be effective to modify separators, but it inevitably decreases the porosity of separator and reduces the efficiency of ion transport [26]. Moreover, optimizing polyolefin separators to increase their thermal stability and decrease simultaneously polarization is rarely reported.

Herein, a new type composite separator was designed by combining the hydrophobic silica aerogel and PP separator. Owing to the rich pores, high thermal insulation, and electrolyte (EC/DMC, DMC/DOL, and Diglyme) affinity of hydrophobic silica aerogel, the composite separator compensated for the inherent defects of PP separator and promoted the separator with good performance. In detail, SAC separator not only maintains high mechanical strength and self-closing control advantages of the PP separator, but also possesses a 3D porous network structure. These special structures can effectively prevent the heat transmission, improves the surface area and surface energy of the separator, which facilitate the movability of the electrolytes. In addition, hydrophobic groups and 3D porous structure of silica aerogel layer together increase the affinity and electrolyte retention ability. As a result, the SAC separator possesses improved thermal stability, cycle stability and better rate performance in LIBs. This work provides a new way to improve the safety and rate performance of power batteries.

2. Experimental

2.1. Preparation of silica aerogel

All of the chemical reagents were commercially purchased, without any treatment before used. The solution of tetraethyl orthosilicate (TEOS, Sinopharm Chemical Reagent Co., Ltd.), ethanol and water with molar ratio of 1:5:5 were added in to a beaker and stirred for 20 min at room temperature. Then 0.1 mol/L HCl was added into the mixture to adjust the pH to 3–4. The pH of the solution was positioned at 6.3 by 1 mol/L ammonia and kept stirring for 6 h. After that, the solution was maintained at room temperature for 12 h to get a gel. The gel was then aged in proper amount of ethanol. The gel was treated at 50 °C with a

mixture of TEOS and ethanol (volume ratio 1:4.5) by 4 h for 3 times, followed by treating at 60 °C with heptane by 4 h for 3 times. Then the gel was further treated with a mixture of trimethyl chlorosilane and heptane with volume ratio of 1:5 for 4 h at 50 °C and repeated for 3 times. Finally, the as-prepared gel was placed at 60 °C for 6 h, 80 °C, 100 °C, 120 °C and 150 °C each of 3 h to get the hyaline sky-blue silica aerogels [27–29].

2.2. Fabrication of SAC separator

The preparation of SAC separators is as follows. The slurry for coating was prepared with the powder of silica aerogel and Polyvinylidene fluoride (PVDF) by using N,N-Dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd.) as solvent (weigh ratio 1:1.3:30). After stirred and ultrasonic treatment thoroughly, the silica aerogel slurry was coated on PP separator. The coated separator was dried at 50 °C for 8 h, and then 70 °C for 12 h, to obtain SAC separator. For comparison, silica ceramic separator was also prepared in the similar procedure with the SAC separator, only the amount of DMF was varied to get a uniform coating.

2.3. Characterization

The crystal structures were characterized by X-Ray Diffraction measurement (XRD, X'Pert PRO) using Cu-K α radiation at a scan rate of 4° min⁻¹. Specific surface area and pore size distribution were measured by automated surface area (ASAP2420-4MP). The morphology was obtained by using Scanning Electron Microscopy (SEM, ZEISS Merlin Compact). Chemical bond and functional groups were confirmed by FT-IR spectrometer (Nicolet iS50). The electrolyte contact angles of the separators with different electrolytes (EC/DMC, DMC/DOL, Diglyme, water and EC/PC) were determined by using a contact angle measurement instrument (Dataphysics OCA20). Thermal analysis of the separators was verified by simultaneous thermal analyzer (STA 449 F3) in a temperature range of 25–200 °C at a heating rate of 5 °C min⁻¹ under argon atmosphere.

2.4. Electrochemical measurements

The electrochemical performance of the prepared separators was tested by assembled coin cells. The cathode was prepared by mixing commercialized LiFePO_4 materials, acetylene black as conductive agent and PVDF as binder with a weight ratio of 8:1:1. A proper amount of NMP was added into the mixture to form homogeneous slurry by stirring, the obtained slurry was coated onto aluminum foil. And then, the cathode was dried at 70 °C for 24 h and 120 °C for 2 h, and tailored into discs with a diameter of 13 mm. Lithium plate was used as the anode, 1 M LiPF_6 in EC/DMC (1:1) as electrolyte. Both SAC separator and PP separator were tested as battery separators, respectively. The batteries were assembled in an argon-filled glove box. The galvanostatic charge-discharge tests were examined at a potential range of 2.0–3.8 V (vs. Li/Li^+) at room temperature using a Land battery test system (Land CT2001A). The cycle voltammetry test was verified by CHI 604e electrochemical workstation with a scanning rate of 0.5 mV s⁻¹ in the voltage range of 2.0–4.3 V. AC impedance analysis was performed by using CHI 604e electrochemical workstation over the frequency range of 100 kHz–0.01 Hz.

The ionic conductivity was measured using a similar sandwich model of stainless steel/separator/stainless steel. The ionic conductivity was measured by AC impedance. The frequency range was 100 KHz–10 Hz, the amplitude was 10 mV and the electrolyte was EC/DMC (1:1). The conductivity is calculated by the following formula:

$$\delta = d/(R \cdot S) \quad (1)$$

δ is the ionic conductivity, d is the thickness of the separator, R is the

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