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Inorganic ceramic fiber separator for electrochemical and safety performance improvement of lithium-ion batteries

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ABSTRACT

A separator based on ceramic fibers with excellent properties, utilized for powerful laminated lithium ion batteries, was prepared by low-cost production process. Physical and chemical characteristics of the separator and the electrochemical as well as the safety performance of lithium ion batteries were extensively investigated, and compared to commercialized polyethylene (PE) and ceramic-coating PE (C-PE) separators. The results demonstrated that inorganic ceramic fiber (CF) membrane exhibited higher porosity (85%), higher electrolyte uptake (381%) and higher ionic conductivity (1.48 mS/cm). Moreover, CF separator did not display thermal shrinkage at 160 °C for 1 h, manifesting that the separator possession of high thermal stability. The lithium nickel cobalt manganese oxide $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/ graphite battery employing the CF membrane displayed superior rate capability, which delivered the discharge capacities of 13.206 A h (0.2 C), 12.729 A h (0.5 C), and 12.074 A h (1 C), respectively. In addition, this battery improved cycle stability, with the capacity retention of 101.4% following 100 cycles at 1 C rate. Results of safety tests presented that batteries with CF separator passed both nail penetration and extrusion tests, implying that the safety performance was remarkably improved. Additionally, CF membrane had only 20 cents in cost for 1 Ah cells, which was ten times lower than commercial PE and C-PE separators. The perfect combination of good properties and low cost made it possible for the CF separator to be a promising separator for laminated lithium-ion batteries, which are especially used in electric vehicles.

1. Introduction

As the demand for high energy density and capacity increase, the safety problems of electric vehicles caused by lithium ion batteries draw a significant public attention [1–3]. The safety of lithium-ion batteries is closely related to the thermal stability of cathode materials, the properties of the electrolytes and the resistance to the elevated temperature of separators [4]. Actually, the temperature-dependent security issues are mostly related to the dimensional shrinking or melting of the separator [5]. As an essential segment of the lithium-ion battery, the separator plays the role of providing pathways for the migration of lithium ions, storing electrolytes for the transfer of ions during charging and discharging cycles, as well as preventing internal short circuits resulted by the direction contact of the cathode and the anode [6]. Although the separator does not participate in any reactions, the corresponding structure and characteristics highly affect the battery performances, including the energy densities, the capacities, the cycle life and the safety [7]. An ideal separator should exhibit the properties of highly porous structure, high electrolyte uptake, high mechanical and electrochemical stability, and high thermal stability for high-performance battery production.

Currently, both the micro-porous monolayer polyethylene (PE) and the polypropylene (PP) separators have been widely utilized in commercialized lithium-ion batteries, due to the corresponding good mechanical properties and chemical stabilization [8,9]. In contrast, the intrinsic properties, such as poor thermal stability resulted by the low shutdown temperature of polyolefin (PE/130 °C, PP/165 °C), low wettability caused by the hydrophobicity of polyolefin and poor electrolyte retention, limit the corresponding application in high power lithium ion batteries [7]. Therefore, the alternative separators towards high thermal stability, good wettability and high electrolyte retention are inevitable.

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Tremendous strategies were executed for these drawbacks to be overcome, including polymer and inorganic modifications. It has been researched that the polymer utilization as the membrane material or the polymer, introduced onto the polyolefin separators or non-woven mats could improve the properties in terms of thermal stability, electrolyte retention and wettability [10–24]. It has been also reported that the polyolefin membrane or non-woven mats modification by similar inorganic particles such as Al_2O_3, SiO_2, ZrO_2 and TiO_2 are proven useful in mechanical strength, thermal stability and ionic conductivity improvements of separators [25–35]. In contrast, the safety demands of the batteries cannot be met, especially the demands utilized for electric vehicles. Based on the issue, the pure inorganic separator was prepared due to the intrinsic high thermal stability of inorganic particles, whereas still many challenges have limited the practical applications, such as the complicated production process and the poor flexibility [36,37]. Furthermore, according to the prices of materials and lithium ion technology, the separators share over 20%. Moreover, the high cost of separators is linked to the production process [5]. Therefore, any further developed candidate separators should combine both excellent properties and low costs.

Consequently, a separator (called ceramic fiber separator (CF)) with superior characteristics, containing high porosity, high electrolyte uptake, high ionic conductivity and super-high thermal stability was obtained by a cost-effective manufacturing process. For comparison, both the PE separator (PE) and the ceramic-coating PE separator (C-PE) were selected as counterparts. Moreover, the electrochemical and safety properties of the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite batteries with the CF membrane as separator were intensively investigated.

2. Experimental section

2.1. Preparation of ceramic fiber separators

The ceramic fiber separator was prepared by a traditional wet winding process. The cheap paper made special ceramic fiber (containing 45–47%Al_2O_3 and 52–54%SiO_2) as the raw materials, the carboxyl methyl cellulose (CMC) as the cohesive material and the polyethylene oxide (PEO) as the dispersant, a certain proportion of the materials (weight ratio of 90:7:3) was dissolved into an amount of distilled water under a continuous stir, whereas the viscosity of the solution was controlled by the binder contents. Following stirring for 8 h, the mixed solution was placed onto the forming wire to form a membrane, followed by overnight drying at 120 °C under vacuum. Consequently, the membrane thickness was controlled by an extended roller (C3385-ZE, China).

The commercial PE and C-PE separators were purchased from the Tianjin DG membrane Technology Company.

2.2. Characterization of separators

The thickness of the membranes was measured with an insertion between two slides by a micrometer caliper. The morphology and microstructure of the separators were analyzed by a scanning electron microscope (SEM, PHILIPS XL30).

The porosity of the separators was measured by the n-butyl alcohol (BuOH) uptake method and was calculated by the following equations [38]:

$$P(\%) = 100 \times (M_w - M_d)/\rho_b V_s \quad (1)$$

$$V_s = \pi r_s^2 \cdot d \quad (2)$$

where M_w and M_d are the weight of the wetted and dry separators, respectively; ρ_b is the density of the n-butyl alcohol (0.81 g cm^{-3}) and V_s is the volume of the dry separator, r_s is the radius of the circular shape, and d is the thickness of the dry separator.

The electrolyte uptake of the separators could reflect the absorption ability of the membranes. The electrolyte uptake was calculated by the following equation:

$$Uptake(\%) = 100 \times (M_1 - M_0)/M_0 \quad (3)$$

where M_0 and M_1 are the weight of the membrane prior to and following the electrolyte absorption, respectively.

The square separators with a length of 6 cm placed between two glass plates were subjected to various temperatures from 90 °C to 160 °C for 1 h, for the heat treatment execution.

In order for the ionic conductivity of the separators to be investigated, a blocking-type cell was fabricated by the electrolyte-soaked membrane placement between two stainless steel electrodes in an Ar-filled glove box. Consequently, the impedance data of the cell was measured by an electrochemical workstation (CHI660E, China) in the frequency range from 0.01 Hz to 10 kHz with an amplitude voltage of 5 mV. Consequently, the ionic conductivity was calculated by the following equation:

$$\sigma = D/RS \quad (4)$$

where S is the contact area of the electrodes, R is the resistance of the separator which can be obtained from the AC impedance date and D is the thickness of the separator.

2.3. Lithium-ion batteries assembly

The lithium ion batteries with a width of 120 mm and a length of 190 mm were assembled through a lamination technology for the electrochemical and safety performance evaluation. The positive electrode with the two-sides area density of ~500 g/m^2 was prepared by coating an N-methyl-2-pyrrolidone(NMP)-based slurry containing the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ materials, polyvinylidene fluoride (PVDF) and Super-P carbon and KS-6 (95:2:1.5:1.5 by weight) onto an aluminum foil. The negative electrode with the double surface density of ~250 g/m^2 was prepared by coating a water-based slurry of graphite, carboxyl methyl cellulose (CMC), Super-P carbon and Styrene Butadiene Rubber (SBR) (95:1.5:1:2.5 by weight) onto copper foil. The positive and negative electrodes were dried at 120 °C for 12 h under vacuum and subsequently were cut into the required size. The ceramic fiber separator was exploited as the separator. The batteries were assembled manually by exploit the three type membranes as the separator and following packaged by an aluminum film. Consequently, the electrolyte (1 M $LiPF_6$ dissolving the mixed solvent of EC and DEC (1:1, v/v)) was injected into the batteries under an Ar-filled glove box. The actual capacity of the battery was approximately 12 A h with a 1.05 capacity ratio of the negative electrode to the positive electrode.

2.4. Electrochemical tests

The effects of various separators on the cycling stability and the rate capability were measured by a computer-controlled battery test system (Neware, China). The rate performances were carried out under a voltage range of 2.7–4.2 V at the current rates of 0.2 C, 0.5 C and 1 C (1 C=12 A). The cycle tests of the batteries were executed at 1 C rate.

2.5. Safety performance tests

For the safety performance investigation of these batteries, the nail penetration and extrusion tests were executed. The nail penetration and the extrusion tests were executed from an impact extrusion needling integrated machine (Baer, China) at room temperature following the cells were fully charged. The nail penetration test was conducted by a stainless steel nail with a diameter of 3 mm at a speed of 50 mm/s for the batteries penetration, whereas consequently the surface temperature and voltage changes versus time were recorded.

The extrusion test was carried out by the following steps. Firstly, the battery was placed between two flats. Consequently the extrusion force

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