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Evaluation of a polymethylpentene fiber mat formed directly on an anode as a battery separator

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ABSTRACT

Battery separator is a porous membrane that separates the positive and negative electrodes to prevent their electrical shorting, yet enables lithium ion transport through the liquid electrolyte in its pores. In this work, a polymethylpentene (PMP) non-woven separator was formed directly on an anode through the electrospinning process. The PMP separator exhibited a much improved thermal dimensional stability compared to a commercial polyolefin separator. It showed negligible shrinkage in the 150 °C oven test, while the shrinkage was close to 55% for a commercial separator in the machine direction. It also enabled good effective ionic conductivity in the range of 1.16–1.44 mS/cm when saturated with the liquid electrolyte of 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:2 by volume). The cell performance was tested in coin cells with the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode and the graphite anode. The cells with the PMP separators displayed stable cycling performance and good rate capabilities. However, the PMP separators showed low tensile strengths and the effect of the low tensile strengths on the performance of large format batteries needs further investigation.

1. Introduction

Battery separator is an electrochemically non-active but critical and costly battery component. It should keep the anode and cathode electrically separated to avoid battery shorting under not only normal, but also abusive operating conditions. Therefore, its mechanical properties and dimensional integrity at high temperatures directly affect the battery abuse tolerance, which is especially important for large format battery applications. The battery separator also enables the lithium ion transport through the liquid electrolyte that fills in its porous structure. Its permeability to lithium ions affects the battery impedance, and a low impedance improves battery rate performance and reduces the heat generated at a high charging and discharging rate, thus extending battery life.

In order to improve the performance of a battery, a separator must fulfill several requirements, such as low thickness, good permeability, thermal stability, and appropriate pore size [1–3]. The majority of the commercial separators for lithium ion batteries are made of stretched polyolefin microporous membranes such as polyethylene (PE) and polypropylene (PP). However, polyolefin-based separators suffer from significant thermal shrinkage, which has raised serious concerns over their ability to prevent internal electrical short circuits under abuse conditions. Ceramic coating on separators can significantly improve their thermal dimensional stability [4–6]. However, if not handled properly, any non-uniform ceramic coating could cause non-uniform current density distribution which is deleterious to battery life as it can lead to localized overcharge and overdischarge conditions. Coating containing hydrophilic ceramic particles could also make the separator drying challenging, as any drying temperature above 100–120 °C can cause permanent morphological changes of the stretched commercial separators. Therefore, high temperature polymers are being evaluated extensively to improve the battery abuse tolerance.

Besides porous polymeric membranes, the other major type of battery separators is nonwoven mats [7–16]. Although non-woven mats have been used as separators for several types of batteries, they have very limited applications in lithium ion secondary batteries. Nonwoven mat separators have certain advantages such as relatively low processing cost, high porosity, heat resistance, and lightweight. However, they typically have inadequate pore structures. There are ways of making non-woven mats, such as the dry laid, wet laid, melt blown, and electrospinning processes. Among them, electrospinning is a versatile process that can creating porous submicron fiber mats by using electrostatic forces to uniaxially stretch a spinning solution as it solidifies [17]. The process requires a high voltage power supply (0–30 kV) applied to the spinning solution. A jet will form when the voltage reaches the critical point at which the repulsive forces in the solution overcome the surface tension in the solution droplet. As the solvent

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from the jet evaporates in mid-air, the electrostatic forces cause the fiber which is being produced to elongate. The final product is collected on a grounded collector and generally takes the form of a nonwoven mat.

Separators made of the electrospinning process have been prepared and evaluated by several research groups [7–12]. Because of their good electrochemical stability and electrolyte affinity, electrospun polyacrylonitrile (PAN) separators have shown great rate capability and the capability to improve the battery cycling performance [7–10]. Electrospun polyvinylidene fluoride (PVdF) mats have also been tested for lithium ion battery separator applications. They exhibited good electrolyte retention and significantly improved rate capability in coin cells [11,12]. Coin cells with these mats displayed high electrolyte uptake resulting from their highly porous structure and good rate performance due to the reduced cell resistance. Generally speaking, electrospun separators enable high rate charge/discharge of lithium ion batteries because of their high porosity and favorable pathways for ion transport (i.e., preponderance of open pores). However, most of the polymers evaluated so far do not have good liquid electrolyte chemical resistance.

In this work, low density polymethylpentene (PMP) mats were deposited directly on graphite anodes. The anode was used as a collector for electrospun fibers as it is electrically conductive. The potential benefits of forming the separator directly on an electrode are (1) a simplified production process and (2) an improved interfacial adhesion between the separator and the deposition electrode. PMP was selected as it has a very low density, excellent resistance to moisture, good chemical and mechanical stability in a liquid electrolyte, and a high melting temperature. The PMP separator coating can be used either alone or together with a commercial separator to provide improved performance, especially thermal dimensional stability.

2. Materials and experimental

Polymethylpentene (PMP) was purchased from Sigma-Aldrich (St. Louis, MO). It has a density of 0.84 g/cm³ and melting temperature of ~235 °C. This medium molecular weight PMP has a melt index of 26 g/10 min (260 °C/5 kg). Analytical grade dimethylformamide (DMF) and cyclohexane were also purchased from Sigma-Aldrich (St. Louis, MO), and used as-received, without further purification.

The electrode materials used in this work were $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Toda NCM-01ST-100) (NCM) for the cathode and TIMREX SLP 30 graphite for the anode. The conductive additive in both electrodes was TIMREX Super P Li carbon black. Kynar HSV 900 PVDF from Arkema Inc. (Philadelphia, PA) was used as the electrode binder.

In order to prepare the separator, PMP was first dissolved in a mixture of cyclohexane and DMF (4:1 by weight), to form a 3 wt% solution through stirring at a slightly elevated temperature. PMP mats were then prepared by electrospinning the warm PMP solution (at about 45 °C). A Glassman high voltage supply was used to supply a 12 kV voltage and a syringe pump (Gemini 88, KdScientific) was used to deliver the PMP solution at a rate of 5 ml/h. The PMP solution was extruded through a 20 gauge needle. Either a calendared graphite electrode or a thin aluminum foil was used as a deposition collector for the electrospun fibers. The distance between the syringe tip and the collector was 12 cm. After fabrication, the mats were compressed on the collectors (electrodes or aluminum foils) at room temperature for 20 s under various pressures, in order to improve their mechanical properties and uniformity. The mats compressed at 0, 1, 2 and 3 MPa are designated as PMP-0, PMP-1, PMP-2, and PMP-3, respectively.

The schematic of forming the separator on an anode is shown in Fig. 1. The PMP fiber mat was electrospun directly on the anode. Once the desired thickness was achieved, an optional calendaring process was followed to improve the mat surface uniformity. The photos and scanning electron microscope (SEM) images in Fig. 1 show the graphite anode and the separator formed on the anode. Note that the calendared anodes exhibited no thickness change after the compression of the PMP-anode assemblies.

The surfaces of the electrospun mats formed directly on the anodes were examined with SEM. The cross-sections of the free-standing PMP mats were also examined by SEM after fracturing the mats in liquid nitrogen.

The apparent porosity of each porous membrane was estimated using the following equation:

$$P = 1 - \frac{w_m}{\rho_p V_a}, \tag{1}$$

where w_m is the mass of the free-standing PMP mat, ρ_p is the density of PMP (0.84 g/cm³), and V_a is the apparent volume of the PMP mat.

Effective ionic conductivities (σ_{eff}) were calculated from the following equation:

$$\sigma = \frac{d}{R_b S}, \tag{2}$$

where d is the thickness of the free-standing membrane, R_b is the resistance of the electrolyte filled separator, and S is the area of the electrode. Membrane samples were filled with a liquid electrolyte (1 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:2 by volume)) and sandwiched between two stainless steel electrodes. R_b was obtained using an electrical AC impedance analyzer.

The tensile properties of the membranes were tested with an Instron 5582 according to ASTM D882-09 at a cross-head speed of 10 mm/min.

The hot oven test and dynamic mechanical analysis (DMA) were used to characterize the high temperature dimensional stability of the separators. Free-standing electrospun mats and a polypropylene (PP) separator (Celgard 2400) were kept in an oven at 150 °C for 1 h and their dimensional changes were recorded. In addition, PMP mats saturated with a liquid electrolyte (1 M $LiPF_6$ in EC/DEC (1:2 by volume)) were tightly sealed in coin cells and similar hot oven tests were conducted at 150 °C for 1 h, to evaluate the high temperature dimensional stability of the separator in the presence of a liquid electrolyte. For the DMA test, strips of different membranes were tested using a tensile clamp. A small load of 0.001 N was applied and the strain was recorded as the temperature increased to 250 °C at a ramp rate of 2 °C/min.

A simplified version of the hot tip test was used to measure the diameter of the hole formed in the separator membrane in response to a hot wire in contact. A 0.6 mm diameter copper wire heated to 250 °C was put in contact with the membrane sitting on an electrode and the diameter of the hole was measured.

The permeability of free-standing mats was tested with a capillary flow porometer (CFP 1100AE) in this work. The air flow rate was recorded as a function of the increase of the air pressure.

Linear sweep voltammetry was used to evaluate the electrochemical stability of the membranes. A membrane sample impregnated with the liquid electrolyte was sandwiched between a stainless steel electrode and a lithium foil, and the assembly was sealed in a coin cell. The cell voltage was swept at a scan rate of 1 mV/second until the onset of current flow.

CR2325-type coin cells were prepared in order to evaluate the electrochemical performance of the cells with different types of separators. The coin cells were assembled with the NCM as the cathode, graphite as the anode, and 1 M $LiPF_6$ in EC/DEC (1:2 by volume) as the electrolyte. The capacities of all lithium ion cells