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Performance evaluation of a non-woven lithium ion battery separator prepared through a paper-making process

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HIGHLIGHTS

- Composite separators have been successfully developed using a paper-making process.
- The composite separators show good thermal stability and electrolyte wettability.
- Cells with the composite separators exhibit good cycling performance.
- The composite separators also enabled excellent cell rate capability.

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ABSTRACT

Porous separator functions to electrically insulate the negative and positive electrodes yet communicate lithium ions between the two electrodes when infiltrated with a liquid electrolyte. The separator must fulfill numerous requirements (e.g. permeability, wettability, and thermal stability) in order to optimize the abuse tolerance and electrochemical performance of a battery. Non-woven mat separators have advantages such as high porosity and heat resistance. However, their applications in lithium ion batteries are very limited as their inadequate pore structures could cause accelerated battery performance degradation and even internal short. This work features the development of thermally stable non-woven composite separators using a low cost paper-making process. The composite separators offer significantly improved thermal dimensional stability and exhibit superior wettability by the liquid electrolyte compared to a conventional polypropylene separator. The open porous structures of the non-woven composite separators also resulted in high effective ionic conductivities. The electrochemical performance of the composite separators was tested in coin cells. Stable cycle performances and improved rate capabilities have been observed for the coin cells with these composite separators.

1. Introduction

Secondary lithium ion batteries appeal to many users because they offer a high specific energy, a high energy density, a long cycle lifetime, a low self-discharge rate, and a high operational voltage [1]. Their four major components are the positive electrode, the negative electrode, the electrolyte, and the separator that is disposed between the two electrodes. The porous separator functions to physically and electrically insulate the negative and positive electrodes yet communicate lithium ions between them when infiltrated with the liquid electrolyte. The separator property is one of the key factors that directly affect the abuse tolerance and electrochemical performance of a battery.

Porous polyolefin membranes are the most widely used lithium ion battery separators due to their good electrochemical and chemical stability, very low moisture absorption, and excellent tensile properties. However, the processes of making conventional separators require precise stretching of the extruded thin film to create pores [2–4]. Heat exposure to these stretched separators initiates re-coiling of the elongated polymer chains, observed as membrane shrinkage, which could significantly increase the risk of battery shorting, especially for large format battery applications. In addition, the melting temperature of polyolefin is normally in the range of 120–170 °C. Any local hot spots developed under abnormal conditions could cause the melting of the separator further increasing the contact area between the two electrodes.

Non-woven mat separators have been widely used in several types of batteries because they normally have high porosity, good chemical resistance, and excellent thermal stability. However, the major barriers to using non-woven separators in lithium ion

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batteries have been their large pore size and the difficulty in making thin (<25 μm) uniform non-wovens. In recent years, non-woven separators made of novel sub-micron sized fibers have been developed and tested in lithium ion batteries [5–12]. Non-woven mats of polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), and polymer blends of polyimide with porosities ranging from 65 to 85% have been prepared with a relatively slow electrospinning process [5–7]. Those electrospun separators have shown negligible shrinkages at elevated temperatures and enabled good ionic conductivities. However, these polymers can be plasticized by liquid electrolytes leading to reduced mechanical properties. Wet-laid or air-laid non-woven fabrics based on thermalplastic polymers have also been evaluated as lithium ion battery separators [8–12]. They exhibited good dimensional stability at elevated temperatures as well as high effective ionic conductivities.

This report discusses the development and performance characterization of cellulose nanofiber based composite separators. A wet-laid process was bench-scaled to prepare the composite separators comprising cellulose fibers and ceramic particles. Cellulose is the most abundant biorenewable material, and natural cellulose fibers have excellent mechanical strength and thermal stability. The ceramic particles have been used to conveniently control the permeability of the composite separators. The other two potential functions of the ceramic particles include improving the non-woven mat uniformity and increasing the mat resistance to dendrite (or metal particle) penetration due to their excellent compressive strength.

2. Materials and experimental

The fiber used in this investigation was Celish micro-fibrillated cellulose (MFC) (Daicel Finechem Ltd) [13]. MFC is a micro-fibrillated cellulose made from highly refined pure plant fibers through a strong mechanical shearing force provided by a super-high-pressure homogenizer. It has a highly branched structure and the fiber diameter can be from 0.1 to 0.01 μm. The ceramic powder was a 1 μm alumina. Technical grade acetone was purchased from Sigma–Aldrich (St. Louis, MO). The anode and cathode materials used to make the full cells were TIMREX SLP 30 graphite and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) (Toda NCM-01ST-100), respectively. The electrolyte used was 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) 1:1 (v/v) (Novolyte Technologies).

The preparation of the MFC composite mats was achieved by a wet-laid (paper-making) process. The schematic is shown in Fig. 1. Controlled amounts of cellulose fibrils and alumina were weighed and mixed in distilled water by a bench scale shear blending for ∼10 s. The uniform dispersions were filtered in a batch process onto two layers of 100 mesh screens and then dried in an oven at 80 °C for 2 h. Upon the careful removal from the mesh, composite mats with thicknesses of >35 μm were obtained. The final step of compressing the mats improved the mat uniformity and increased their mechanical properties. The mats were compressed under a pressure of 3 MPa for 20 s at room temperature between two parallel plates on a 50 Ton PHI hand press (SRPRSS-8004). The composite separators were then dried at 120 °C overnight before the characterization of their properties. In addition, the pressed mats were coated with porous polyvinylidene fluoride (PVDF) (Kynar® 761) by dipping in a coating bath consisting of a solution of 0.6 g of PVDF dissolved in a mixture of 0.4 g of distilled water and 14 g of acetone. A porous PVDF structure was formed with the evaporation of acetone via the well-known phase inversion process. The PVDF coating was added to augment the separator mechanical strength, keep ceramic particles from falling off, and improve the separator surface uniformity. The coated composite mats were then dried at 120 °C overnight for characterizations.

The surface morphologies of the composite mats were examined using a scanning electron microscopy (SEM). Samples were sputter coated with gold and exposed to an accelerating voltage of 5 kV.

The separator porosities were estimated using the equation below:

$$P = \frac{w_T - w_s}{\rho_l \cdot V_s}$$

where w_s is the weight of the dry separator sample, w_T is the weight of the separator once a liquid is fully absorbed, ρ_l is the density of the liquid, and V_s is the apparent volume of the sample.

The air permeability of the free-standing mats was tested on a capillary flow porometer (CFP 1100AE). The air flow rate was recorded when ramping up the air pressure to 250 kPa.

The tensile properties were tested on an Instron 5582 test frame according to ASTM D882-09. The strain ramp rate was 50%/minute.

The membrane wettability by a liquid electrolyte (1 M $LiPF_6$ in EC/DMC (1:1 by volume)) was performed by carefully applying a drop of the electrolyte on the membrane and observing its spread in 1 min.

The membrane thermal performance was evaluated using a dynamic mechanical analyzer (DMA Q800, TA Instruments) and a hot tip test. For the DMA tests, a preload force of 5 mN was applied and the temperature was ramped from 30 to 250 °C at a rate of 2 °C min^{-1}. Commercial polypropylene (PP) samples (Celgard 2400,

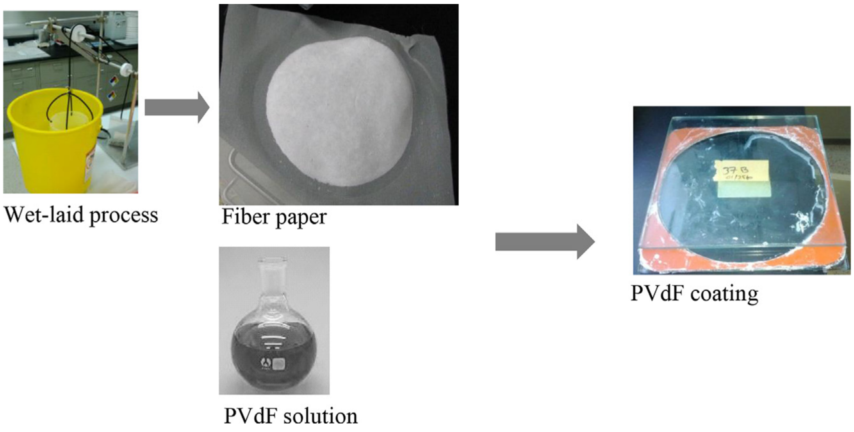

Fig. 1. Schematic of the preparation of the composite mats.