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Mechanical behavior and failure mechanisms of Li-ion battery separators☆

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HIGHLIGHTS

- Mechanical behavior of three types of Li-ion battery separators investigated.
- Strain rate sensitivity studied in two orthogonal directions.
- Inhomogeneity of strain distribution determined by digital image correlation.
- Separators show very different failure modes and strength.

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ABSTRACT

Anisotropic mechanical properties were experimentally determined and compared for three types of commercially available Li-ion battery separators: Celgard 2325, Celgard PP2075 dry-processed polymer separators, and DreamWeaver Gold 40 non-woven separator. Significant amount of anisotropy of properties was determined, with the Young's modulus being different by up to a factor of 5 and ultimate strength being different by a factor of 10 between orthogonal directions within a polymer separator layer. Strain rate sensitivity was investigated by applying strain rates ranging from $1 \cdot 10^{-4}$ s^{-1} to 0.1 s^{-1}. Significant strengthening was observed and the strain rate strengthening coefficients were determined for both elastic modulus and yield stress in case of polymer separators. Digital image correlation technique was used to measure and map the strains over the specimen's gage section. Significant strain concentration in bands running perpendicular to the tensile axis was observed in polymer separator samples oriented in transverse direction. Such localized necking allows for extremely high strains close to 300% to develop in the material. The failure mode was remarkably different for all three types of separators which adds additional variable in safe design of Li-ion batteries for prevention of internal short circuits.

1. Introduction

Successful electrification of automotive drivetrains depends in large part on improvement of safety of on-board energy storage systems, which nowadays are almost exclusively represented by lithium-ion secondary batteries assembled in packs. These systems store significant amount of energy and the rapid release of it, such as in the event of a short circuit, can lead to catastrophic events such as thermal runaway. In a liquid electrolyte-based Li-ion cell of any shape factor the charge is transported between the electrodes by ions, while the electrons carry the charge through the electrodes, metal current collectors, and to the external circuit. The component that prevents the electronic current occurring between the electrodes, i.e. prevents the direct contact between them, is termed a separator. This component thus should address the following requirements: a) it should be porous to allow liquid electrolyte to carry lithium ions, and b) it should have sufficient

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strength to prevent contact between the electrodes. The latter is typically assessed by a puncture strength parameter. There are also additional requirements such as low thermal shrinkage.

The second requirement (mechanical strength) is the primary subject of the present study. Currently two major measures are used to address this: Young's modulus in machine direction (MD) and puncture strength [1]. Machine direction is chosen for dry processed separators since it is the direction of windings during jellyroll processing and thus the material should withstand tension from winding machine. The puncture test follows the ASTM D4830 standard [2] which describes puncture strength as a maximum load applied to a needle with 1 mm tip radius at a penetration rate of 0.5 mm/s. The current requirements are 100 MPa for the Young's modulus and 300 g for puncture strength [3].

While the above parameters may be sufficient to address integrity of separators during battery manufacturing and transport, they do not provide a full understanding of mechanical behavior of these membranes. For instance, as demonstrated in the current report, the elastic modulus of polymeric separators appears to be a function of loading rate, which is not reflected in a 100 MPa requirement. Better understanding of mechanical properties of separators is especially relevant when the behavior of the battery under external mechanical loading (such as in the event of crush or drop) is considered. Constitutive models describing mechanical behavior of separator can be used in numerical models for better predictions of battery response and improvements in safety [4,5]. In addition, during battery charging and discharging, separator can deform due to swelling of electrodes and thus change the effective properties in terms of ionic conductivity [6].

There are number of studies on Li-ion battery separators addressing the mechanics that have been published relatively recently [7–12]. The early study [7] first reported changes in porosity due to mechanical load and investigated the separator safety shutdown mechanism as a function of temperature. In other reports, tensile and compressive experiments on commercial separators have been discussed [8–12]. Such experiments usually involve a single type of separator, often extracted from a commercial Li-ion cell after its disassembly [4,5] and thus providing limited knowledge of the separator type, manufacturer, and its composition. Most studies involve polymer separators, for example Celgard 3501 in Ref. [12] or Celgard C480 in Ref. [9]. Both dry and wet experiments in compression were performed in Ref. [12] and the poroelastic model was subsequently proposed in Ref. [13] to describe the effect of liquid filling the separator pores under compression. The probably most comprehensive study is reported in Ref. [11] where separators from three manufacturers were tested for crack propagation under tension in different directions with in-situ atomic force microscopy (AFM). Finally, thermomechanical behavior of several polymer separators was studied in Ref. [10].

The current investigation expands the existing knowledge of mechanical behavior of porous membranes used as Li-ion battery separators by: i) comparing the behavior of three different materials (viz. Celgard 2325, Celgard PP2075, and DreamWeaver Gold 40); ii) investigating anisotropy and strain rate sensitivity; iii) investigating inhomogeneity of strain distribution under tensile loading and fracture mode. For that purpose, two porous polymer membranes manufactured by Celgard LLC and one nonwoven separator manufactured by Dream Weaver Inc were tested under wide range of strain rates. Digital image correlation (DIC) technique was used to observe strain distribution in samples as the test progressed. In addition to reporting basic mechanical properties of the materials, such as elastic modulus and yield stress, the paper discusses significant differences in strength, strain distribution, and failure mode among the three materials, which may provide guidance for addressing the safety of Li-ion batteries.

2. Experiments

MTS load frame with 50 lbs (~0.2 kN) load cell with 0.1 N measurement accuracy was used for the experiments. Wedge grips were used to hold the sample; rubber inserts were placed inside the grips to prevent tearing of separator (Fig. 1). Samples were 8 cm long strips with width equal to 2 cm. The gage length was kept at 40 mm. Samples were cut from the as received sheets of separator material using razor blade. Tests were done under displacement control, dry conditions. Strain rates ranging from $1{\cdot}10^{-4}$ s^{-1} to 0.1 s^{-1} were applied. Based on the reports on the measurements of Li-ion pouch cell swelling during electrochemical cycling, the lower strain rate may be considered as corresponding to 1C cycling of a $LiCoO_2$ vs Graphite pouch Li-ion cell [12]. Here the term C-rate is used and C indicates the time required to completely charge or discharge the battery, i.e. 1C represents charge in 1 h and 0.5C would correspond to charge in 2 h. Digital image correlation was used to measure the strain distribution. The speckle pattern for DIC was made manually by using a permanent marker ink. The decision was made to use this method rather than commonly used spray painting technique due to possible alteration of properties of separator by paint or delamination of paint during the test. VIC 2D software was used for image analysis and calculation of strains. A small tensile load of approximately 0.1 N was applied prior to test to keep the sample straight and avoid any droop. The reference image for DIC was recorded in this initial state. Microstructure of separators was observed using Hitachi S-4800 field emission scanning electron microscope (FE-SEM) using 5 kV accelerating voltage. A thin layer of gold was sputtered on the samples to avoid charge build up in SEM.

Three types of separator were tested: Celgard 2325, Celgard PP2075, and DreamWeaver Inc 40 μm thick microfiber-based separator. Their description is arranged in Table 1 (porosity and thickness was determined by the corresponding manufacturer). Commercial films were obtained from Celgard LLC and Dreamweaver International and were used in as-received condition. Two Celgard separators were chosen to study the difference between triple-layer and single-layer polymer membranes. While 2325 separator has three layers of Polypropylene/Polyethylene/Polypropylene (PP/PE/PP), the PP2075 is a high-porosity single PP layer, developed by Celgard for high-rate applications. The DreamWeaver Gold40 is a non-woven sheet made of Kevlar-type (para-aramid) fibers with very high porosity (Table 1). All of the experiments were conducted at room temperature in ambient atmosphere. Tensile behavior was determined in two orthogonal directions, as shown in Fig. 2(b). It is expected that there is a certain degree of anisotropy due to the separator manufacturing procedure and the properties in machine direction (MD) differ from those in transverse direction (TD).

3. Results and discussion

Comparison of tensile strength of the three separators is provided in Fig. 2(a). The results shown in Fig. 2(a) correspond to $1{\cdot}10^{-3}$ s^{-1} strain rate. Significant difference in behavior can be observed with the polymer separators displaying high anisotropy while the fiber-based DreamWeaver behaves isotropically. It is interesting to note that tensile strength of a single-layer Celgard PP2075 is higher than that of the triple-layer Celgard 2325. Overall, the ratio of the tensile strength in MD over tensile strength of TD is close to a factor of ten for Celgard 2325 and is higher for Celgard PP2075. This ratio remained constant for all applied strain rates used in the experiments. Such anisotropic behavior is consistent with expectations for dry processed polymer separators for