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Measurement of the through thickness compression of a battery separator

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HIGHLIGHTS

- A capacitance based displacement set-up has been developed for thin film testing.
- The through thickness compression was measured for sample as thin as 50 µm.
- PP separator, NMC cathode, and PP/NMC/PP stack were tested in air and in DMC.
- PP separator shows a softer through thickness compressive response in DMC.
- Response of the stack agreed with the rule of mixture prediction up to 0.16 strain.

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ABSTRACT

The mechanical integrity of the separator is critical to the reliable operation of a battery. Due to its minimal thickness, compression experiments with a single/a few layers of separator are difficult to perform. In this work, a capacitance based displacement set-up has been developed for the measurement of the through thickness direction (TTD) compression stress-strain behavior of the separator and the investigation of its interaction with the electrode. The experiments were performed for a stack of two layers of Celgard 2400 separator, NMC cathode, and separator/NMC cathode/separator stack in both dry and wet (i.e. submersed in dimethyl carbonate DMC) conditions. The experimental results reveal that the separator compression modulus can be significantly affected by the presence of DMC. The iso-stress based rule of mixtures was used to compute the compressive stress-strain curve for the stack from that of the separator and NMC layer. The computed curve agreed with the experimental curve reasonably well up to about 0.16 strain but deviated significantly to a softer response at higher strains. The results suggest that, in the stack, the TTD compressive deformation of the separator is influenced by the NMC cathode.

1. Introduction

Battery separators are porous thin films that prevent physical contact between the positive and negative electrodes while enabling ionic transportation. The integrity of the separator is vital to the electrochemical performance as well as the abuse tolerance of a battery. To predict the integrity of the separator under thermal, mechanical and other abuse conditions in numerical simulations, the stress-strain response of the separator is a required input [1–3].

Thin films usually have an anisotropic microstructure and their stress-strain responses depend strongly on orientations. Fig. 1 presents a three-dimensional (3D) representation of a typical single layer polypropylene (PP) separator Celgard 2500 [4]. The PP separator is considered as an orthotropic material with three material directions referred to as the machine direction (MD), the transverse direction (TD), and the through thickness direction (TTD). The mechanical properties of the separators are commonly measured in tension in the two in-plane directions, i.e. MD and TD [2,5–8], and in compression in TTD [1,9–12]. Due to its thin thickness, compression experiments with a single layer or a few layers of separator are difficult. It requires a displacement measurement with a submicron resolution and a high parallelism in loading. Limited by the resolution of conventional displacement measurement methods such as the linear variable differential transformers (LVDT), the compression measurements have been performed with a stack of 32, 40 and 224 layers of separator [1,9,11,12]. For commercial separator with MD and TD directions, the samples need to be carefully aligned in the same direction in the stack to avoid the trapping of thin air layers between the layers to ensure the measurement accuracy. Nanoindentation is another technique which has been used for such measurements. Nanoindentation can achieve a

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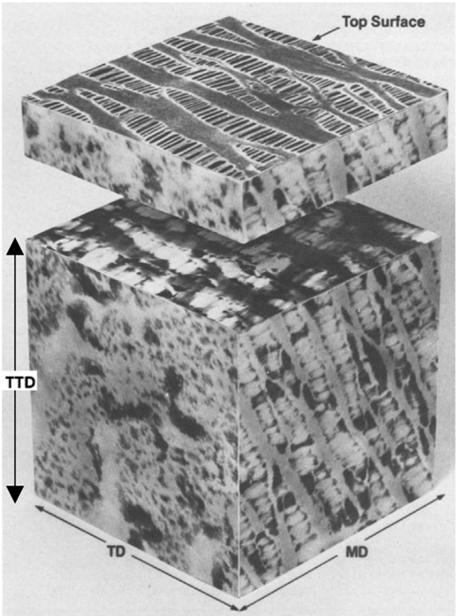

Fig. 1. 3D Representation of Celgard 2500 [4], a typical single layer PP separator. The three material directions are referred to as MD, TD, and TTD.

high resolution in TTD displacement measurement. However, as the radius of the indenter tip is comparable to the size of the microscopic features of the separators, the measured property depended on the locations of the indentation [13]. In addition, the nanoindentation measures the surface properties, not exactly the bulk properties in the TTD. For the purpose of the quick screening of separator materials and the accurate measurements of the material stress-strain responses, it is desirable to have a technique to measure the compression response using a single layer/a few layers of separator.

In the literature, a number of techniques have been investigated for thin film thickness measurement, including the capacitance based displacement measurement technique [14–19], prism coupling technique [20], hydrostatic strain measurement technique [21], picosecond laser ultrasonics [22], and Brillouin light scattering technique [23]. Compared to other methods, the investment for the experimental set-up with the capacitance technique is relatively low, and the capacitance sensor can be incorporated in a compression test as demonstrated in the measurement of the elastic modulus of solid films of 75 µm [14] and 4–20 µm thicknesses [16].

The current work investigates the TTD compression of battery separators using a capacitance based displacement measurement technique. The compression experiments have been performed on a Celgard 2400 separator, a $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) cathode and a separator/cathode/separator stack. The experiments were carried out in air and in dimethyl carbonate (DMC).

2. Experiment

2.1. Capacitance based displacement measurement system

To measure the TTD displacement of thin films, a capacitance based measurement set-up has been developed in house. Fig. 2 presents the experimental set-up. The main component is a pair of parallel discs made of precision glass. The disc has a diameter of 50.8 mm, thickness of 6.35 mm and a surface flatness ½ wavelength (~0.3 µm) at its smooth side. The discs are used as the compression platens for mechanical loading and as the capacitor plates. The capacitor electrode covers a circular area of 24 mm diameter at the center of the discs. It is a thin layer of tungsten coating of 5 nm thickness created by plasma sputtering. The electrical connection to the electrode is via a 3 mm wide conductive path created by tungsten coating on the disc. In the assembly shown in Fig. 2c, the two paths on the two discs were oriented at opposite directions with no overlap. Evidently, they did not contribute to the capacitance.

To maintain the parallelism of the glass discs, three small circular shaped samples will be tested simultaneously. This self-alignment method has been demonstrated in Ref. [16]. The samples will be placed between the two glass discs, outside the electrode measuring area and in equal spacing as shown in Fig. 2. The samples are 3 mm in diameter, having the same distance of 19 mm from the disc center. For easy sample positioning, three 3 mm × 3 mm square marks have been created on the glass discs by plasma sputtering of a tungsten layer of 5 nm thickness.

The capacitance displacement measurement set-up will be used in air or in solvent conditions. The solvent used here is DMC, a common solvent in electrolyte for lithium-ion batteries. When testing in a solvent, the glass discs and sample assembly will be put into an Al container and the solvent will be added to submerse the assembly.

The capacitances were measured by a LCR meter Extech 380193. The applied AC voltage was 0.5 V with a frequency of 1 kHz. The capacitance data was recorded every 2 s through a built-in RS-232 interface with a data acquisition software. The accuracy of the capacitance measurement was ± 0.1 pF.

For a parallel plate capacitor, the capacitance C depends on the distance between the two plates t

$$C = (\varepsilon_0 \varepsilon A)\frac{1}{t} \quad (1)$$

where ε_0 is the permittivity in vacuum, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m; ε is the relative permittivity of the dielectric medium between the plate; and A is the area of the parallel plate capacitor. The value of ε in air is 1.00059. For DMC, the reported ε value was between 3.08 and 3.12 [24]. In the current work, $\varepsilon = 3.10$ was used.

For the set-up in Fig. 2, ± 0.1 pF corresponds to a displacement of ± 0.015 µm to ± 0.73 µm for a sample thickness ranging from 25 µm to 170 µm in air. In DMC, the resolution in displacement measurements is about three times higher.

2.2. Samples

Three types of samples have been tested. These are Celgard 2400 separator, NMC cathode, and separator/cathode/separator stack.

Celgard 2400 separator is a microporous polypropylene (PP) membrane with a nominal thickness of 25 µm. The NMC cathode used in this work is a double-side coated electrode on a 20 µm aluminum collector with a total nominal thickness of 110 µm. It was made in house. Fig. 3a and b shows the surface images of the Celgard 2400 separator and the NMC cathode, respectively.

In a battery cell, the separator is sandwiched between electrodes and is stretched during the cell assembly process. The cell is slightly compressed when being assembled in a battery pack, and may be subjected to further compression during battery charging/discharging cycles [25], or in the event of impact [3,10]. To evaluate the effect of electrode roughness on the separator, a stack configuration of PP/NMC/PP was also tested, where PP represents one layer of Celgard 2400 separator and NMC represents the NMC/Al current collector/NMC of 110 µm thickness. The nominal thickness of the stack is160 µm.

All samples were cut using a hammer driven hole puncher. The samples were 3 mm in diameter. Fig. 3c shows three types of samples prepared by this way. For samples with multiple layers of anisotropic separator, folding prior to cutting can help to orient the layers in the same direction [9].

2.3. Loading

The compression experiments were performed using a MTS Insight