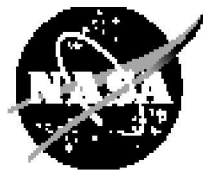


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# Battery Separator Characterization and Evaluation Procedures for NASA's Advanced Lithium-Ion Batteries

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## **Abstract**

To address the future performance and safety requirements for the electrical energy storage technologies that will enhance and enable future NASA manned aerospace missions, advanced rechargeable, lithium-ion battery technology development is being pursued within the scope of the NASA Exploration Technology Development Program's (ETDP) Energy Storage Project. A critical cell-level component of a lithium-ion battery which significantly impacts both overall electrochemical performance and safety is the porous separator that is sandwiched between the two active cell electrodes. To support the selection of the optimal cell separator material(s) for the advanced battery technology and chemistries under development, laboratory characterization and screening procedures were established to assess and compare separator material-level attributes and associated separator performance characteristics.

## **Introduction**

As NASA embarks on a renewed human presence in space, safe, human-rated, electrical energy storage and power generation technologies that will demonstrate reliable performance in a variety of unique mission environments will be required. NASA Constellation Program elements include the Crew Exploration Vehicle (Orion), crew and cargo launch vehicles (Ares I and Ares V, respectively), the Lunar Surface Access Module (Altair), extravehicular activity (EVA) surface suits and extraterrestrial rovers and habitats (Ref. 1). To address the future performance and safety requirements for the energy storage technologies that will enhance and enable these and other future aerospace missions, advanced rechargeable, lithium-ion battery technology development is being pursued within the NASA Exploration Technology Development Program's (ETDP) Energy Storage Project, with an emphasis on addressing performance technology gaps between state-of-the-art capabilities and critical future mission requirements.

Lithium-ion batteries have not been fully space-qualified for use as a main energy storage element for manned, human-rated aerospace missions. Currently, both cell and cell component development efforts are focused on improving the overall safety, as well as the electrochemical attributes, of such battery systems in order to optimize their performance for manned space applications. A key cell component of a lithium-ion battery which significantly impacts both of these performance features is the battery separator.

The function and reliability of the separator is critical for the optimal performance and safety of a lithium-ion cell. In nonaqueous, liquid-electrolyte cells that exemplify a lithium-ion cell chemistry, the separator is typically a non-electrically-conducting porous electrolyte-filled media or membrane, which is sandwiched between and in contact with the two active, solid electrodes. Its roles are to prevent direct electronic contact between the two electrodes that would result in a short-circuit and to allow the flow of ionic species within the cell. Certain separator materials can function as internal cell safety devices. The separator affects the internal cell resistance, stability, cycle-life, operating temperature range and cell kinetic parameters such as discharge and charge rates. By its ability to regulate the electrolyte distribution between the active electrodes, as a result of its morphology and permeability characteristics, the separator limits ionic diffusion and recombination rates, and, thus, impacts cell capacity, power and available energy. With respect to the inherent safety of a lithium-ion cell, the separator may afford passive protection and tolerance to cell abuse conditions that may arise, and it can enhance the overall cell safety by providing another level of internal redundancy.

The structural and physiochemical properties of the separator material strongly influence the overall cell performance, although the separator does not “actively” participate in the battery operation. The mere presence of the separator component within a cell adversely affects the overall cell performance, as it adds electrical resistance and occupies limited space. For electrochemical cell chemistries in which the liquid electrolyte solution serves only as an ionic conductor, the separator should be as thin as possible and porous, but yet possess the required physical strength to maintain the mechanical and electrical separation between the solid electrodes. These characteristics are essential in order to achieve high energy and power densities for applications requiring such performance attributes. Thus, the practical design of a separator is an art, as there is a compromise between the degree of porosity of the material and its mechanical strength. For battery safety, a state-of-the-art battery separator for utilization with lithium-based cell chemistries should have the inherent ability to shut the battery down if overheating occurs. Several comprehensive reviews of battery separators in general (Refs. 2 and 3) have appeared in the literature, as well as some with a primary emphasis on lithium-based cell technologies (Refs. 4 and 5). Recently, a NASA applications-focused summary review was prepared which elucidated primary separator properties and characteristics for rechargeable lithium-based cells, how the separator properties influence cell performance and safety and how degradation of the separator component may result in overall cell failure (Ref. 6).

Within a focused Separator Development subtask of the NASA ETDP’s Energy Storage Project, a complementary effort was instituted in-house to define, develop and validate separator screening test procedures which would address standard cell-level performance as well as abuse conditions.

### **Separator Screening Procedures Selection Methodology**

To define and establish appropriate cell separator component material laboratory characterization and screening procedures, which will be utilized as part of a portfolio of standard procedures to compare and select optimal components for the ETDP lithium-ion cell development project, a set of material performance and/or property profiles for a particular separator material was created. A specific profile is defined as a set of standard experimental protocols (procedures) for evaluating the key cell component critical properties which influence the specific performance attribute being addressed. Profiles for separator component screening and evaluation are grouped as follows:

- Baseline material composition / morphology
- Electrical performance
- Mechanical performance
- Thermal performance

Critical separator material properties are those that can impact the performance of a practical cell in either a positive (beneficial) or a negative (detrimental) way. A single material property may affect

multiple cell performance attributes, or, conversely, multiple material properties may collectively affect a single cell performance attribute. A matrix approach was utilized to first identify the critical separator material properties and understand how they affect or relate to cell performance, followed by the prioritization of the material properties/parameters of primary interest, particularly those that could influence multiple practical performance attributes.

The approach utilized to establish and validate standard laboratory evaluation procedures for each profile was based upon following or modifying ASTM or other existing procedures, e.g., procedures developed within NASA under the Polymer Energy Rechargeable System (PERS) program or those employed by others in the technical field, as well as methodologies that could be accomplished with available in-house capabilities.

An advantageous screening procedure would be one that addresses a specific material critical “performance” property that would be a function of more than one material property (e.g., separator resistivity would be dependent upon thickness, permeability, porosity, tortuosity, etc.). Another advantage would be the utilization of a common “test fixture” or experimental setup that would be applicable for multiple test procedures. Each procedure would be documented utilizing a standard “template” architecture, which are included in the Appendices. In the following section, specific separator component screening and evaluation procedures and methodologies belonging to each of the profile groupings are described in detail.



# Portfolio of Material Performance and Property Profiles

## 1.0 Baseline Material Composition/Morphology Profile

Key chemical and physical properties of the separator material will be evaluated, as appropriate, in order to characterize the material with respect to chemical composition, surface morphology, wettability and chemical inertness.

### 1.1 Thickness

#### 1.1.1 Purpose

This procedure documents methods for measuring separator thickness. The separator thickness is a critical property that affects mechanical strength, cell impedance, energy density and rate capability.

#### 1.1.2 Scope

It is essential that a separator specimen has uniform thickness and assured contact with both electrodes while not allowing contact between the two electrodes. Thickness values should be minimal to allow increased conductivity of a cell, but not compromise mechanical strength. The desired thickness for separators in lithium-ion applications is less than 25  $\mu\text{m}$ .

#### 1.1.3 Equipment

Sample thickness shall be measured to a precision of  $\pm 0.0005$  in. A Mitutoyo Series 543 digital indicator, or equivalent, shall be used. Care must be taken to assure that the separator sample is not distorted or crushed when making the thickness measurement. The Series 543 gage has a 2 Newton (N) force limit and will exert a pressure of less than 25 kPa (4 psi) when fitted with a 3/8 in. diameter tip. Always use a flat tip with large area. A sharp or radiused tip can “sink” into the material and produce a false, low reading for thickness. Thickness is to be measured in enough places to determine sample uniformity and to identify a mean sample thickness.

#### 1.1.4 Procedure

##### 1.1.4.1 Sample Inspection

1. Become acquainted with the MSDS sheets and special handling requirements for the materials that make up the separator sample. Read and follow any special handling precautions.
2. Obtain a blank “Thickness Data Form” for the sample to be tested.
3. Date and initial the form and record sample ID, including Lab Notebook references if applicable.
4. Record a detailed physical description including:
  - a. Appearance (color, clarity, evidence of non-uniformity such as bubbles, blisters etc.)
  - b. Physical characteristics (e.g., tacky, soft, very sticky etc.)
  - c. Surface texture (rough, shiny etc.)

##### 1.1.4.2 Measuring and Calculating Mean Thickness

- a. Turn on the micrometer using the ON/OFF button. If the display does not indicate that the measurement is zeroed, press the ZERO/ABS button.
- b. Change the units to mm (if not already in this mode) by pressing the in/mm button.
- c. Trim a piece of separator material 10 cm long and 10 cm wide.
- d. Measure and record the sample thickness in at least four places around the perimeter and once near the center of the sample. Use care to assure that the surface of the separator is not damaged in making these measurements.
- e. Note the minimum and maximum sample thickness on the data sheet.

- f. Calculate the mean thickness of all five measurements and record on data sheet.

### 1.1.5 Analysis and Results

Results are tabulated, and a mean material thickness along with the precision of the multiple measurements is reported.

## 1.2 Scanning Electron Microscopy (SEM)

### 1.2.1 Purpose

This procedure documents an instrumental method for characterizing separator morphology, material consistency and uniformity. Material uniformity and consistency are critical parameters that ensure homogeneity and unvarying production of separators. Uniformity and consistency influence separator performance because defects, cracks, holes and irregularities are unwanted characteristics, not exhibited by viable baseline material.

### 1.2.2 Scope

Material characterization methods are based on scanning electron microscopy (SEM), and resulting electron micrographs are visually interpreted. SEM theory and more advanced interpretation techniques are beyond the scope of this procedure.

The procedure imposes a high energy beam of electrons upon the surface of the sample and measures how many secondary electrons are knocked off the sample by the scanning high energy beam of electrons. The final image is built up from the number of electrons emitted from each spot on the sample. The image is in black and white and depicts a three dimensional image of the sample.

The material under test must be electrically conductive. The test described in this procedure is designed to use electrons to determine the structure of the sample and therefore must be sputter-coated with a thin layer of gold.

It is preferable that lithium-ion battery separator samples be tested as freestanding films (i.e., not bonded to a substrate or carrier).

### 1.2.1 Equipment

Illustrations are specific to the HITACHI S-3500N SEM instrument, operated in conjunction with its HITACHI S-3500N software. The sputter coater fixture and methods can be applied with instruments such as those available from EMITECH K550X using an Edwards vacuum pump in conjunction with Argon gas.



Figure 1.—Hitachi S-3500N scanning electron microscope.

## 1.2.2 Procedure

1. Cut two samples from different areas of the separator and mount them on the sample holder with carbon tape.
2. Coat the sample with gold using sputter coater (Emitech K550X)—current of 25 mA for 60 sec.
3. Turn on and operate the SEM (Hitachi S-3500N) for material sample scans and data handling according to the instrument operation manual.
4. Examine the two samples. Treat them as two samples if they look different.
5. For each sample:  
Set accelerating voltage to 5kV.
  - a. Capture images at x500 and x5k magnifications at 45° tilt.
  - b. Capture images at x100, x500, x2k, 5k, 10k, and 20k magnifications.
  - c. Capture more images that may be of interest.

## 1.2.3 Analysis and Results

### 1.2.3.1 Interpretation of Data

1. Upon evaluation of images, look for inconsistencies, faults, cracks or other deformations that should not be present within the film and take note of them
2. Describe the type of surface texture present.
3. If comparing a fresh and used sample, be sure to note any differences in surface topography that are present.

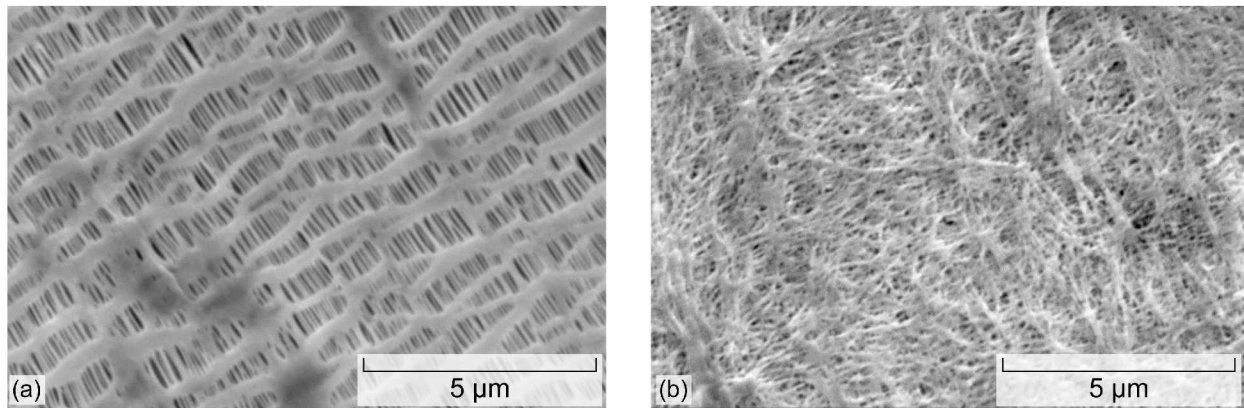


Figure 2.—Scanning electron 10 k micrographs. (a) Celgard 2500 separator made by a dry process. (b) Tonen separator made by the wet process. Separator samples were sputter-coated with gold to provide better resolution by reducing electrostatic charging.

## 1.3 Fourier Transform Infrared Spectrometry (FTIR)

### 1.3.1 Purpose

This procedure documents methods for measuring separator chemical composition. Characterization of the separator material chemical composition enables possible determination of certain characteristics like mechanical robustness, melt integrity and thermal shutdown properties of separators.

### 1.3.2 Scope

Techniques for measuring the chemical composition of lithium-ion battery separators are described. The methods are based on Fourier Transform Infrared Spectroscopy (FTIR). A simple, infrared spectroscopy method of absorptions and vibration of bonds allows for interpretation of the graphical representation of these changes to determine chemical composition is presented. FTIR theory and more advanced interpretation techniques are beyond the scope of this procedure.

The procedure emits photons (light) from the infrared portion of the electromagnetic spectrum, 4,000 to 375  $\text{cm}^{-1}$ , to the sample. The bonds in the sample will either absorb the light at that frequency or it will cause the bonds to vibrate. Analysis of these absorption characteristics reveals details about the molecular structure of the sample.

It is preferable that lithium-ion battery separator samples be tested as freestanding films (i.e., not bonded to a substrate or carrier).

### 1.3.3 Equipment

Nicolet Nexus 670 spectrometer instrument, operated in conjunction with Nicolet's OMNIC software.

### 1.3.4 Procedure

#### 1.3.4.1 Checking the Nitrogen Purge Gas

1. Be sure to check the amount of nitrogen being supplied to the FTIR setup. It should be between 20 and 40 psi and the flow meter should read approximately 30 standard cubic feet per hour (SCFH).
2. Never use a flammable gas or argon to purge the spectrometer. The purge gas must be free of moisture, oil, carbon dioxide and other reactive or infrared-absorbing impurities.



Figure 3.—Thermo Nicolet Nexus 670 FT-IR.



### 1.3.4.2 Checking the Desiccant

1. Check the humidity level inside the spectrometer at least once a month, when in use, to protect the optics.
2. Click the Check Desiccant button on the Diagnostic tab of the Experiment Setup dialog box.
3. If the existing humidity level exceeds the factory-specified limit, a warning message will inform you to replenish the desiccant.
  - a. Mount a piece of sample with adhesive tape on a sample card.
  - b. Turn on and operate the FTIR (ThermoNicolet Nexus 670) according to the instrument operation manual.
  - c. Select the Default -Transmission Experiment
  - d. Look through the sliding door of the main chamber to make sure no sample is in the sample holder.
  - e. Collect background spectrum.
  - f. Insert the sample card in the sample holder in the main chamber.
  - g. Wait for 2 min to purge the chamber.
  - h. Collect a spectrum of the sample.
  - i. Search the library for matching spectrum.

### 1.3.5 Analysis and Results

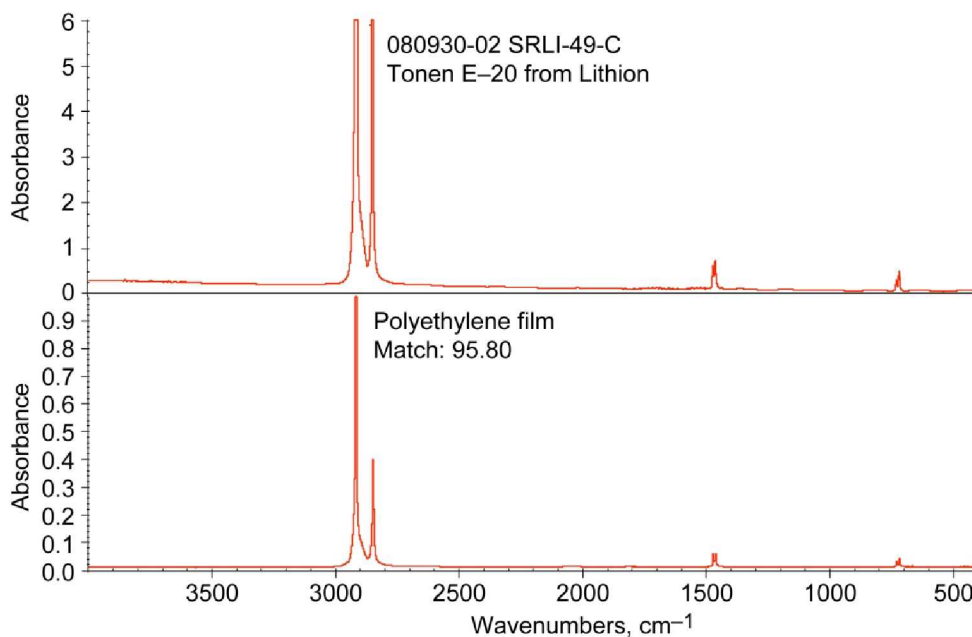


Figure 4.—FTIR spectrum of a Toner E-20 separator, matched well with the spectrum of a polyethylene film.

## **1.4 Separator Wettability**

### **1.4.1 Purpose**

This procedure documents methods for measuring separator wettability, which is a material property that controls the amount of electrolyte retained in the separator. If there is insufficient separator wetting, this could lead to drying of the separator in the cell and possibly cause dimensional changes. Wettability influences relative permeability and electrical properties.

### **1.4.2 Scope**

The methods are based on testing how fast a standard electrolyte solution wicks into the separator. A simple drop test method for interpreting the wettability data is presented. Wettability, or wetting, is the actual process when a liquid wets (spreads) on a solid substrate. Contact angle theory and more advanced interpretation techniques are beyond the scope of this procedure.

The procedure imposes a drop of a standard electrolyte upon the surface of the sample and measures how quickly the liquid is absorbed into the open pores of the separator. It is essential that the specimen has uniform thickness and length. Per vendor literature, optimal microporous separator samples for lithium-ion cells should be  $\leq 25 \mu\text{m}$  in thickness and  $< 1 \mu\text{m}$  in pore size diameter.

It is preferable that lithium-ion battery separator samples be tested as freestanding films (i.e., not bonded to a substrate or carrier). However, if the sample is bonded to a carrier, then the visual observation may still be carried out.

### **1.4.3 Equipment**

#### **1.4.3.1 Sample Holder**

A household aluminum foil or a rigid plastic sheet serves as a holder and support for the polymeric material under testing and provides protection for the work surface from the standard testing electrolyte. The aluminum foil or plastic should be big enough to allow ample space for the specimen and needed tools.

#### **1.4.3.2 Thickness Measurement Device**

Sample thickness shall be measured in accordance with the characterization procedure in Section 1.1, as previously described.

#### **1.4.3.3 Low-Moisture Enclosure**

Lithium battery electrolytes such as the 1:1 by volume mixture of ethylene carbonate: dimethylcarbonate containing 1 M  $\text{LiPF}_6$  contain moisture sensitive materials. It is imperative that the standard electrolyte be kept dry. This can be achieved by testing the separator in either a glove box or in a dry-room atmosphere. When testing outside of a controlled atmosphere environment, a sealed container with desiccant shall be used to protect the testing electrolyte.

## **1.4.4 Procedure**

### **1.4.4.1 Sample Inspection**

1. Obtain a blank "Wettability Data Form" for the sample to be tested.
2. Follow the SAMPLE INSPECTION procedure detailed in Section 1.1, but utilizing a blank "Wettability Data Form" for the sample to be tested.
3. Note if sample is freestanding or bonded to a carrier sheet. If the sample is not freestanding, carefully remove the sample from the carrier if this can be done without damage or contamination of the surfaces.

#### **1.4.4.2 Sample Preparation and Mounting**

1. Examine the sample to find a representative area with uniform thickness.
2. Trim a piece of material to 28- by 28-mm so that it is large enough to visually observe changes that take place upon the surface of the separator as the material is wetted.
3. Measure the thickness of the trimmed sample in at least four places around the perimeter and once near the center of the sample. Use care to assure that the surface is not damaged in making these measurements.
4. Note the minimum and maximum sample thickness on the data sheet.
5. Place the sample upon the aluminum foil/plastic work area.

#### **1.4.4.3 Microscope Options**

1. If applicable, place the work area underneath the eye of the microscope to visually see the change on the sample from the microscope at a microscopic level.
2. This is an option to see the changes upon the surface of the polymer sample.

#### **1.4.4.4 Preparing for a Test**

1. In a glove box or dry-room atmosphere, maintain a temperature that is close to room temperature at 25 °C.
2. Place the sample with the work area underneath a microscope or upon a flat surface.
3. Use a micropipette to pipette out 10  $\mu\text{L}$  of a typical electrolyte such as the 1:1 by volume mixture of ethylene carbonate: dimethylcarbonate containing 1 M  $\text{LiPF}_6$ .
4. Assure that the sample temperature is stable ( $\pm 0.1$  °C). Record the temperature of the environment near the sample with an accurate digital thermometer.

#### **1.4.4.5 Running a Test**

1. Release the 10  $\mu\text{L}$  of a typical electrolyte from the micropipette onto the 28- by 28-mm separator sample film.
2. Begin timing when then electrolyte is released to determine visually how long before the sample in its entirety is completely wetted out on the surface.
3. When the sample visually appears to be completely wet, stop recording the time.
4. Record the time needed to wet the sample on the data form.

#### **1.4.5 Analysis and Results**

If the sample fully wets in a set amount of time (e.g., within 2 to 3 sec), then the separator has good wettability properties, as compared to current state-of-the-practice separator materials employed in lithium-ion cells.

### **1.5 Separator Chemical/Electrochemical Stability**

#### **1.5.1 Purpose**

Separators in lithium-ion cells are exposed to an extremely reducing environment at the cell anode (e.g., lithiated carbon) interface and an extremely oxidizing environment at the cathode interface. The separator should be inert to both these extremes, as well as to cell electrolyte solvents and salts, thus, it should not degrade and lose mechanical strength or produce impurities which interfere with the function of the battery. Poor oxidation resistance can result in both poor high-temperature storage performance and poor long-term cycling behavior. Polyolefins, which are universally utilized in lithium-ion cells, have proven stable over long periods.

### **1.5.2 Scope**

A viable approach to verifying separator stability is to perform calendar life testing on complete prototype full-cells containing active electrodes, and then removing the individual cell components for visual and instrumental analyses. Electrochemical oxidation of the separator material could be accelerated by employing a high-voltage cathode material.

### **1.5.3 Equipment**

For separator sample surface inspection and chemical composition, the specific equipment identified in Section 1.2, and in Section 1.3, can be employed.

For cyclic voltammetry, electrochemical instrumentation identified in the experimental procedures developed for the NASA “PERS” program (Ref. 7) can be employed.

### **1.5.4 Procedure**

In the event that a novel experimental polymeric material with unknown bulk stability is desired to be screened with respect to such at the material component level, this could be qualitatively assessed by either (1) studying the surface and/or bulk morphology via SEM and the chemical composition via FTIR before and after prolonged exposure to the desired simulated chemical or electrochemical environment and/or by (2) employing cyclic voltammetric techniques.

A cyclic voltammetry (CV) method can be employed to assess the voltage “window” of electrochemical stability of an electrolyte-imbibed separator to oxidation at high electrode potentials, and the pertinent experimental details of such were formulated as part of a prior NASA program focused on solid polymer electrolyte development (Ref. 7). The CV technique cycles cell voltage linearly over time via a potentiostat and at a constant rate and between specified endpoints. Current flow changes in response to voltage. A graph of current vs. potential is monitored during the test. At potentials where reactions occur, the current will increase in proportion to the rate of reaction, producing a peak in the current vs. voltage plot.

It is essential that the sample be tested as a freestanding film (i.e., not bonded to a substrate or carrier), and the electrodes (e.g., lithium metal and platinum metal) in the test cell must be in intimate contact with the electrolyte-imbibed separator material.

### **1.5.5 Analysis and Results**

For separator sample surface inspection procedures, apparent visual observations of material deterioration, discoloration, pitting, etc. should be documented. For chemical composition studies, changes in spectral characteristics from standard materials would be indicative of degradation. Further detailed characterization of material properties that can affect electrical performance (e.g., porosity) and/or safety (e.g., mechanical integrity) can be performed, as required.

For cyclic voltammetry studies, detailed analyses of the current vs. potential curves will elucidate the nature of electrochemical oxidation and/or reduction reactions that may be occurring between the polymeric separator and the electrolyte.

## 2.0 Electrical Performance Profile

The separator property of a low electrical resistance, which is a function of multiple material properties, has a pronounced effect upon such cell properties as capacity, rate performance, fast-charging capability, overall cell resistance and cycle life.

For safety concerns, the advantages of utilizing a thin separator possessing low electrical resistance must be weighed against the reduction in mechanical integrity, and the cell design should reflect such.

A critical functional separator property is its **permeability**, as the presence of a solid separator material significantly increases the effective resistance of the ion-conducting electrolyte. Permeability is a measure of the ability of a porous material to transmit a fluid, i.e., the liquid electrolyte solution in a lithium-ion cell. The permeability is related to the material's porosity and **tortuosity**, which is the ratio of mean effective capillary length to the separator thickness. Although an air permeability method could be used to characterize the separator permeability, **electrical resistance** or modern ac impedance measurements are more comprehensive for the separator in an actual electrochemical cell environment. Data from such measurements are useful performance indicators, as they describe a voltage loss within the cell during discharge and afford a measure of rate capabilities. The air permeability method is most useful for quality control purposes where rapid determination of lot-to-lot variability is the principal concern.

### 2.1 Separator Ionic Conductivity (Resistivity)

#### 2.1.1 Purpose

This procedure documents methods for measuring separator conductivity. Conductivity is a critical property that controls ohmic losses in batteries. Conductivity influences power capability and waste heat generation.

#### 2.1.2 Scope

Techniques for measuring the conductivity of lithium-ion battery separators are described. The methods are based on electrochemical impedance spectroscopy (EIS). A simple, graphical method for interpreting the impedance data is presented. EIS theory and more advanced interpretation techniques are beyond the scope of this procedure.

The procedure imposes a controlled voltage gradient across the thickness of the sample and analyzes the current flow. It is essential that the specimen have uniform thickness and assured contact with both faces of the test cell.

It is preferable that lithium-ion battery separator samples be tested as freestanding films (i.e., not bonded to a substrate or carrier).

#### 2.1.3 Equipment

Procedures are specific to the Solartron 1250/1286 instruments, operated in conjunction with Scribner Zplot software, v. 2.3.

##### 2.1.3.1 Conductivity Cell

The conductivity cell serves as a holder for the material under test and provides controlled sample dimensions. Conductivity cells usually consist of two parallel, planar electrodes of equal size, but other geometries are possible. The electrodes must be chemically inert and resist the absorption of ions from the material under study. Stainless steel, nickel and sometimes platinum are used for lithium ion electrodes.

Coin cells, also known as button cells, are used in this procedure as the conductivity cell fixture for measurements of lithium-ion battery separators over a range of temperatures. A typical coin cell, as shown in Figure 5, slides into a commercial holding fixture fitted with electrical leads in order to perform the electrical measurements on the cell.



Figure 5.—A typical coin or button cell configuration.

If irreproducible impedance measurements are observed, an alternative to using a commercial coin cell fixture is to carefully spot-weld flat metal sheet tabs to the coin cell's flat conductive surfaces following the cell assembly. This alternative current-conducting configuration can instill improved mechanical integrity with respect to the electrical leads and eliminate the occurrence of detrimental high contact resistances at the cell location.

#### **2.1.3.2 Thickness Measurement**

Sample thickness shall be measured in accordance with the characterization procedure in Section 1.1, as previously described. The separator sample should maintain adequate contact with the coin cell electrodes without excessive sample compression after the coin cell is sealed.

#### **2.1.3.3 Low-Moisture Enclosure**

As mentioned previously, lithium battery electrolytes contain moisture sensitive materials, and it is imperative that the cell components be kept dry. This can be achieved by oven-drying components, as deemed necessary, followed by assembling the coin cell in a glovebox or dry-room atmosphere.

#### **2.1.3.4 Impedance Measurements**

The conductivity of the electrolyte-imbibed separator is calculated from the resistance and dimensions of the sample, and the resistance is most accurately determined by electrochemical impedance spectroscopy (EIS).

This procedure is based on the Solartron 1250 frequency response analyzer coupled to a Solartron 1286 electrochemical interface. The operation of these instruments is automated using Scribner and Associates Zplot and Zview software for Windows (Microsoft Corporation).

Instrument setup and operation is computer-controlled by the Zplot program. Instrument settings are automatically made by opening the ESP conductivity setup file. The automatic settings will work in most instances.

The raw data generated by ZPlot is stored in text file format and can be opened and viewed using text editing software or Microsoft Excel. Impedance data can be quickly analyzed using Zview software.

#### **2.1.3.5 Temperature Measurement/Control**

Conductivity is strongly dependent on temperature, changing by as much as an order-of-magnitude over 20 °C. Phase changes (e.g., melting) within the sample can alter the mechanism of conductivity and produce dramatic changes in conductivity. As such, it is essential that the temperature of the fixture and material be at steady state before measuring conductivity.

Conductivity is measured as a function of temperature. Most of the materials tested have low thermal conductivity and will take 2 to 3 hr to reach a steady state. The experimenter should monitor temperature with time to assure that the sample has equilibrated to within 0.1 °C.

A Tenney environmental chamber is ideal for controlling sample temperature. Provisions for connecting electrical and temperature monitoring leads need to be in place before testing. Shielded

connections must be used in conjunction with guidelines in the Solartron/Schlumberger manual. The conductivity cell must be sealed in a test jar to minimize contamination while under test.

**Caution! Liquid electrolytes usually contain flammable solvents and should not be heated in an atmosphere that supports combustion. Never expose flammable liquids inside the Tenney environmental chambers, as most of these chambers are not rated as explosion proof.**

## 2.1.4 Procedure

### 2.1.4.1 Assembling the Coin Cell

The coin cell can and internal parts should be inspected and cleaned with solvent in a dry-room environment, and the coin cell can should be properly labeled with a scribing tool. Following the thickness measurement of the punched separator sample disc, all components are transferred to an inert-atmosphere glovebox for cell assembly.

A commercial coin cell pneumatic crimper is used to seal the coin cell while inside the inert-atmosphere glovebox after the addition of sufficient liquid electrolyte to completely wet the separator sample and after the correct stacking sequence of the coin cell internal parts. After the coin cell is crimp-sealed and inspected, it can be removed from the glovebox for impedance measurements in an ambient environment.

### 2.1.4.2 Impedance Measurements

The coin cell is to be placed in the Tenney environmental chamber with electrical and temperature-monitoring leads connected appropriately. Usually, conductivity will be measured over a range of temperatures. Stability of sample temperature during a sweep is essential. Make sure the sample is equilibrated by observing the temperature before making measurements.

1. Set the Tenney to the desired target temperature and allow the sample to equilibrate. This will take approximately 3 hr.
2. Assure that the sample temperature read on the Tenney digital temperature readout is stable ( $\pm 0.1$  °C). Record the temperature on the data form.

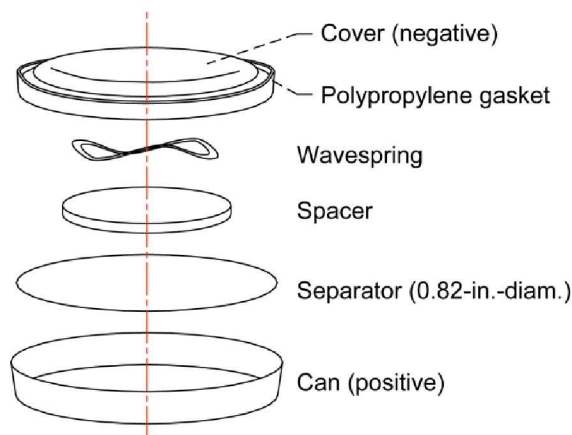


Figure 6.—Coin cell component stacking sequence.

As mentioned earlier, this EIS procedure is based on the Solartron 1250 frequency response analyzer coupled to a Solartron 1286 electrochemical interface, and the operation of these instruments is automated using Scribner and Associates Zplot and Zview software for Windows. Instrument setup and operation is computer-controlled by the Zplot program. Instrument settings are automatically made by opening the ESP conductivity setup file. The automatic settings will work in most instances. The specific operating procedures for the impedance measurements have been well-established and documented during the NASA “PERS” program for solid polymer electrolyte development, and these procedures should be referred to for the separator impedance measurements utilizing the coin cell fixture (Ref. 7).

The Solartron measures the impedance of the sample over a range of frequencies. The instrument will control voltage amplitude, “E”, and sweep frequency. The frequency range swept will vary depending upon material and other cell variables, but a frequency range of 0.1 to 10 kHz could be employed for an experiment designed to fully characterize the material. Often, a single frequency measurement (e.g., 1 kHz) is satisfactory for material screening purposes. At this frequency, the separator impedance is assumed to be equal to the separator resistance. Voltage is controlled between the reference electrode terminals, RE1 and RE2. Current flows between the working and counter electrode terminals, WE and CE. The four-wire design of the fixture helps to minimize errors measuring the cell voltage with non-current carrying leads.

After completion of the desired conductivity measurements, the coin cell can be utilized for future separator evaluations, such as the response of sample resistivity to increasing temperature, as will be described in Section 4.2.

#### 2.1.5 Analysis and Results

The frequency sweep produces a set of data points that make up an impedance spectrum. The spectrum is analyzed to determine the bulk resistance of the sample. Bulk resistance is a function of sample conductivity and cell dimensions. Since the cell dimensions are known, the sample conductivity can be calculated.

The raw data generated by ZPlot is stored in text file format and can be opened and viewed using text editing software or Microsoft Excel. Impedance data can be quickly analyzed using Zview software. The specific Zview software-based analysis and interpretation of the experimental impedance measurement data have been well-established and documented during the prior NASA “PERS” program for solid polymer electrolyte development, and these procedures should be referred to for the separator impedance measurements utilizing the coin cell fixture.

Representative results of separator conductivity measurements as a function of temperature are shown in Figure 7. Such a representation is useful for evaluation mechanisms of conduction and ionic transport and “activation energies” associated with such. Data can also be utilized to estimate the tortuosity and permeability characteristics of the separator material.

In terms of electrical resistivity (i.e., the inverse of conductivity), a microporous separator saturated with electrolyte will have a resistivity of ~6 to 7 times that of the volume of electrolyte that is displaced by the sample. In terms of conductivity, typical values for separators employed in medium-power lithium-ion cells would be  $>1 \times 10^{-3}$  S/cm, where  $S(\text{seimens}) = 1/\Omega$  ( $\text{ohm}^{-1}$ ).



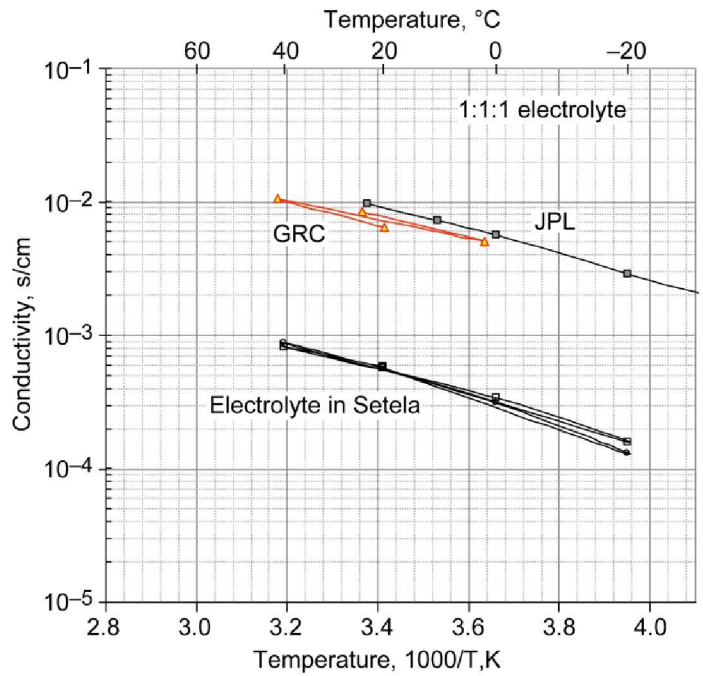


Figure 7.—Conductivity data for a baseline Tonen (Setela) separator compared to free liquid electrolyte.

## 3.0 Mechanical Performance Profile

For safety concerns, the advantages of utilizing a thin separator possessing low electrical resistance must be weighed against the reduction in mechanical integrity, and the cell design should reflect such.

External mechanical abuse on a cell (e.g., “nail” penetration or crush) or an internal short-circuit could result in an abnormal increase in cell temperature, which could seriously compromise safety. If an undesirable cell overcharge condition occurs, dendritic lithium metal could form, which could penetrate the separator as well as causing a drastic reduction in thermal stability.

Overall **mechanical strength** of the separator is characterized in terms of several factors, with each possessing desired requirements and performance metrics. Modern instrumental methods, such as Dynamic Mechanical Analysis (DMA) (Ref. 8), can be utilized for determining both separator material rheological properties and the mechanical integrity of a separator material at elevated temperatures to enhance the screening and evaluation of safety performance.

### 3.1 Separator Puncture Strength

#### 3.1.1 Purpose

If particulate material from the electrodes penetrates the separator, an electrical short may result. Unfortunately, the susceptibility of separators to particle penetration cannot be easily characterized. There is some evidence indicating that penetration resistance correlates with puncture strength, which is the weight that must be applied to a needle to force it completely through a separator. This procedure documents methods for measuring separator puncture strength.

#### 3.1.2 Scope

Techniques for measuring the puncture strength of separators are described. Puncture strength is the weight/force that must be applied to a needle or probe to force it completely through a separator. It is used to indicate the tendency of separators to allow short circuits in a cell that may occur due to holes generated in the separator by the rough surface of an electrode during the battery assembly and charge-discharge cycle. If particulate material from the electrodes penetrates the separator, an electrical short will occur and the battery will be rejected. The puncture strength should be at least 300 grams-of-force per mil of thickness (g/mil) for lithium-ion cells.

#### 3.1.3 Equipment

The procedure utilizes a blunt tip on the end of a digital force gauge which will record the force at which the separator is punctured while slowly moving the tip into the material using a hand wheel motored test stand.

Illustrations are specific to the Imada DS2 force gauge (20 N or 2 k-of-force (kgf) capacity), operated in conjunction with accompanying penetrating pins and the vertical hand wheel test stand.

##### 3.1.3.1 Force Gauge

The Imada DS2-4 Force Gauge is a simple but precise tool that can be used to measure the puncture strength of a separator. It has a special “peak” mode which allows the capture of the peak force achieved during a test which will be the maximum strength the separator can withstand before the pin punctures the separator and the force reading returns back to zero.

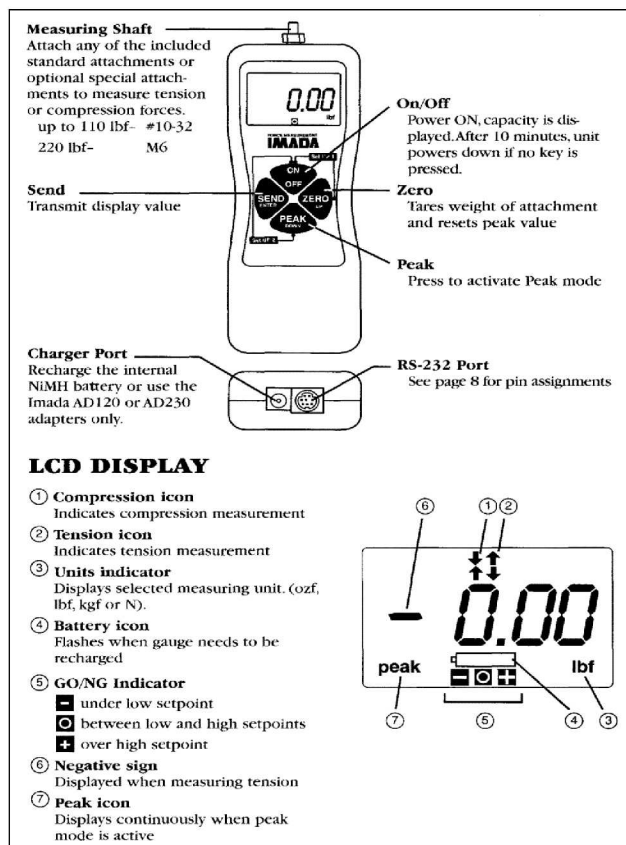


Figure 8.—Images of DS2-4 force gauge display.

Some important cautions to note when using the force gauge include:

1. Do NOT exceed the capacity of the gauge (20 N or 2 kgf). At 110% of the rated capacity, the display will flash to warn the user. Never exceed 200% of the rated capacity or the load cell will be permanently damaged.
2. Always wear eye protection when using the force gauge.
3. The gauge can be used between 0 and 40 °C.
4. Measure in line tension and compression forces only. Never attempt to measure forces at an angle to the measuring shaft, as permanent damage to the load cell will occur.
5. Hand tighten all attachments. Do not use tools.
6. Use only the Imada AD120 charger to recharge the gauge's internal power system.

### 3.1.3.2 Penetrating Pin

The penetrating pin (Model PG-2) is an attachment specially made for the Imada force gauges. It has a 2 mm wide diameter and a blunt and geometrically reproducible end. It easily screws into the force gauge and is used to puncture the separator material.

### 3.1.3.3 Hand Wheel Test Stand

The hand wheel powered test stand (Model HV-110) is a device that allows the force gauge to produce a slow and controlled puncture through the separator. The force gauge can easily be mounted to the stand using the screws supplied with the stand.

It is important to note that the maximum load of the test stand is 100 lbf and the maximum clearance is 9 in. The test stand has an upper and lower travel limit which can be adjusted by loosening the M5



Figure 9.—Force Gauge with penetrating pin installed mounted onto hand wheel test stand.

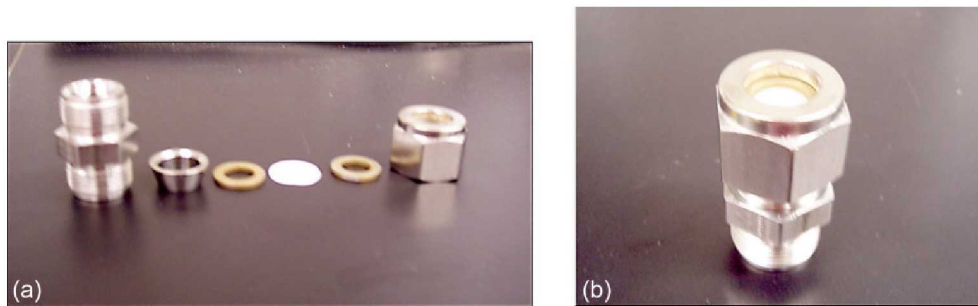


Figure 10.—(a) Parts of separator clamping device. (b) The assembled device.

screw, moving it to the desired position, and retightening the screw. Makes sure that the lower travel limit is set high enough to allow adequate clearance for the force gauge and pin apparatus, so it will not be overloaded. For more detailed instructions or questions, see the HV-110 Instruction Manual.

### 3.1.3.4 Separator Clamping Device

The device that holds the separator taugt and with no dimensional flaws during testing is very important to the reproducibility of the puncture strength test. The clamping device was made in house and consists of a Swagelok ½ in. tube fitting with an accompanying nut, two 5/8 in. washers, and a front ferrule.

Parts from left to right in Figure 10 and order of fitting from bottom to top include: ½ in. tube fitting, front ferrule, 5/8 in. washer, separator sample, 5/8 in. washer, and nut to go on top of tube fitting.

## 3.1.4 Procedure

### 3.1.4.1 Mounting a Sample in the Clamping Device

1. Disassemble the clamping device with a wrench and lay out the parts as in Figure 10(a).

2. Using the punch to cut separators and electrodes for coin cells, make a new circular (0.82in. diameter) separator sample.
3. Place the front ferrule on top of the tube fitting so that it fits easily into the fitting.
4. Place and center the circular separator sample between the two washers and place this sandwich on top of the front ferrule in the tube fitting.
5. Make sure that all parts are centered and then place the nut on top of the tube fitting with all other parts in it and screw the nut into the fitting tightly with a wrench to assure the sample does not slip in any dimension. After assembly, the device should appear as in Figure 10(b).
6. Place the device with separator sample inside in the center of the base plate of the test stand.

#### **3.1.4.2 Running a Test**

7. Ensure that the force gauge is firmly screwed into the test stand and that there is proper clearance for testing. Also ensure that the penetrating pin is firmly screwed into the force gauge but not too tightly. All attachments should only be hand tightened.
8. Turn the force gauge on by pressing the ON/OFF button. The LCD display will briefly show the gauge capacity then zero with a measuring unit. To ensure that the force gauge is in units of kgf, turn off the gauge using the ON/OFF button. Hold the ZERO button and press the ON/OFF button once. Press the ZERO button to cycle through the units. Once kgf is selected, press the SEND button to accept.
9. The force gauge must be in “peak” mode to display the maximum force measured during testing (puncture strength). To do this, press the PEAK button. The word ‘Peak’ will appear in the display when the force gauge is in this mode. The Peak reading will not change until a higher value is measured.
10. If necessary, press the ZERO button to tare the weight of the penetrating pin and shaft.
11. Move the hand wheel so that the penetrating pin and force gauge slowly approaches the sample in the clamping device. The wheel should be moving at a rate of 1 revolution per second. This can easily be achieved by counting “One Mississippi, Two Mississippi, etc.” and ensuring that the wheel is turned one revolution after every second.
12. Keep moving the hand wheel at this specific rate until the penetrating pin has completely punctured the separator sample and a peak value is displayed on the force gauge’s display.

Repeat this procedure as many times as needed for an accurate analysis of the data.

#### **3.1.5 Analysis and Results**

Results are tabulated, and a mean puncture strength force along with the precision of the multiple measurements is reported. Relative comparisons of different separator materials can be made when the same equipment and procedure are employed.

### **3.2 Thermal Shrinkage (Vacuum Oven Method)**

#### **3.2.1 Purpose**

This procedure documents methods for measuring the thermal shrinkage of lithium-ion battery separator materials. Lithium-ion batteries can be poisoned by water, and therefore materials going into a cell are typically dried at 80°C under vacuum. Under these conditions the separator must not shrink significantly and certainly must not wrinkle. The requirement of <5% shrinkage after 60 min at 90 °C (in vacuum), is a reasonable generalization.

### 3.2.2 Scope

The procedure employs measuring the sample's initial dimensions and then placing the sample in a vacuum drying oven at 90 °C for 60 min. The final dimensions are then measured and shrinkage is then calculated from the change in dimensions as shown in the following equation:

$$\text{Shrinkage(\%)} = \frac{L_i - L_f}{L_i} \times 100 \quad (1)$$

where  $L_i$  is the initial length and  $L_f$  is the final length of the separator in both the machine direction (MD) and transverse direction (TD) after high-temperature storage. Most separators will slightly shrink in the MD but will exhibit no shrinkage in the TD.

### 3.2.3 Equipment

#### 3.2.3.1 Separator Samples

To increase the ease of cutting numerous separator samples, a 25-cm long by 25-cm wide piece of sturdy cardboard can be used as a template for cutting samples.

The test specimens shall be two pieces of the separator, 25-cm long and 25-cm wide cut with the aid of the template, one from either of the two transverse edges and one from the center of the sheet as shown in Figure 11. Each specimen shall be marked to show the directions of extrusion (MD) and calendaring (TD). The midpoint of each edge shall be marked for use as a reference point when final measurements are made.

#### 3.2.3.2 Heavy Paper Sheets

A multitude of heavy paper sheets, approximately 40-cm wide by 40-cm long dusted with finely ground talc are needed to hold the samples safely within the oven during the drying process. Note: The paper should be well dusted, and the samples should not be restricted either by the paper or the clips. It is imperative that the samples be free to change shape as strains are relieved during the period of testing.

### 3.2.4 Procedure

#### 3.2.4.1 Vacuum Oven Drying

- a. Cut separator samples according to Figure 11 using the sample template.
- b. Place each separator sample on the heavy paper that has been lightly dusted with talc, and cover with a second piece of dusted paper. Fasten the papers together with paper clips.
- c. Place the paper-separator sandwiches horizontally in the oven. Sandwiches must not be stacked, as this may restrict movement of the separator between the papers.
- d. Set the oven's temperature set point to 90 °C. For detailed instructions, see the VOH-300 Vacuum Oven Operating Manual. Once the oven reaches and equilibrates at 90 °C, set a timer for 60 min and allow the separator samples to remain in the oven for those 60 min.
- e. At the end of the 60 min oven-exposure period, allow the oven to properly cool down and reach a normal pressure. Remove the papers and measure the final length of each side to the nearest 0.25 mm.
- f. Record the results on the data form in the appendix and follow the directions below to calculate percent shrinkage.

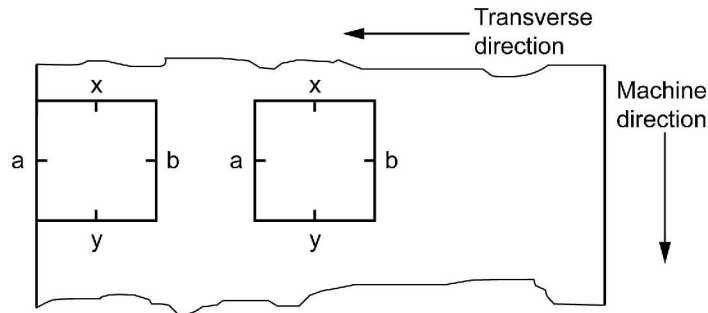


Figure 11.—Method of cutting and labeling test specimens from larger separator sample.

### 3.2.5 Analysis and Results

#### 3.2.5.1 Calculations

- a. Calculate the percent shrinkage using Equation (1).
- b. A negative value denotes shrinkage and a positive value indicates expansion. Measurements should be made and shrinkage should be calculated in each direction (MD and TD) for each sample.

Results are tabulated, and a mean shrinkage along with the precision of the multiple measurements is reported for both directions.

### 3.3 Thermal Shrinkage (DMA Instrumentation Method)

#### 3.3.1 Purpose

This procedure documents an alternate method for measuring the thermal shrinkage of lithium-ion battery separator materials.

#### 3.3.2 Scope

The procedure employs placing a separator sample in a Dynamic Mechanical Analyzer (DMA) under a very low constant force that will simulate holding the sample without placing any kind of tension on it. The temperature is ramped to 90 °C and then held isothermal for 1 hr. The displacement of the sample is measured and serves as a strong indicator of the shrinkage in the particular direction the sample is tested in.

Since the DMA can only measure shrinkage in one dimension, this test must be run in both the machine direction (MD) and transverse direction (TD). Also, even though the DMA cannot apply a vacuum to the sample, as is required in the ASTM D1204-07 procedure, the DMA is located within a dry room which prevents contamination of the separators by water. The humidity level is normally less than 1% within the dry room.

#### 3.3.3 Equipment

##### 3.3.3.1 TA Instrument's Q800 DMA

The Q800 DMA instrument incorporates unique technology to provide the ultimate in performance, versatility, and ease-of-use. State-of-the-art non-contact, linear drive motor technology in the DMA instrument provides precise stress control. Ultra-sensitive optical encoder technology is used to measure strain and air bearing technology insures virtually friction-free movement. The Q800 DMA instrument operates over a wide temperature range (−150 to 600 °C) and provides multiple modes of deformation including dual/single cantilever and 3-point bending, tension, compression, and



Figure 12.—TA Instrument's Q800 DMA with accompanying computer.

shear. The clamps are individually calibrated for data accuracy and the elegant but simple design facilitates sample mounting. If any questions or problems arise, see the Online Help/Operating Manual which can be accessed by selecting “Help” in the TA Explorer Software .

To measure thermal shrinkage the film tension clamp will be utilized. An extremely low constant stress will be applied while ramping temperature to 90 °C and then holding it isothermal for 1 hr while measuring and recording displacement of the sample.

### 3.3.3.2 Separator Sample

A rectangular separator sample can easily be cut with a razor blade in either direction. Ensure that the sample is between 3 to4 mm wide and around 10 to 12 mm long and has straight edges. Remember that this test must be performed in both MD and TD to determine shrinkage in both directions.

**Note: Gloves should be worn at all times when handling the DMA or separator samples to ensure no contamination or degradation of the machine or clamp occurs.**

### 3.3.4 Procedure

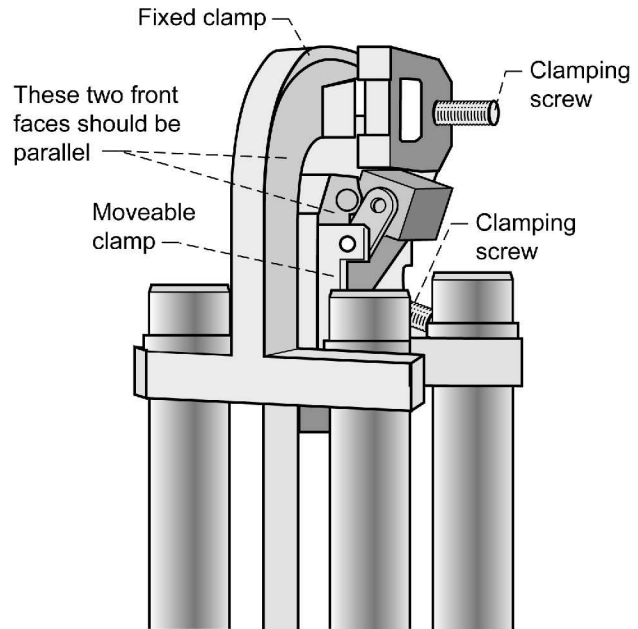
**Note: Before beginning the procedure, ensure that the film tension clamp has been properly installed on the DMA and calibrated. Also ensure that other calibrations (instrument, position, temperature) have been performed. For details, see the TA Instrument's Q800 DMA Calibration Manual.**

#### 3.3.4.1 Loading the Sample in the Film Tension Clamp

1. Press the **DRIVE** key on the instrument to release (float) the clamp.
2. Move the moveable clamp to the approximate position of the desired specimen length. The sample length can be directly observed as a signal output on the instrument display.



3. Press the **DRIVE** key to lock the clamp in position. (The actual specimen length is Measured by the DMA by using the **MEASURE** key after the specimen is mounted.)
4. Loosen the clamping screws on the moveable and fixed clamps (see the illustration to the right for the location of the clamping screws).
5. Slide the sample in from the side of the fixed clamp, then lower it down into the moveable clamp.
6. Push the moveable clamp shut using your finger, then adjust the sample so that it is centered and aligned vertically on the clamp. Make sure that there is no sample underneath the clamping screw. Finger-tighten the clamping screw.
7. Using the torque wrench, tighten the bottom clamp screw on the moveable clamp to the appropriate clamping torque [2 to 3 in.-lb (20 to 40 cm-N) for rigid materials]. Use of excessive torque will bend the stage, causing permanent damage. Use the torque wrench as directed and do not exceed specifications.
8. Carefully align the film so that it is vertical and evenly tensioned across the sample width. Tighten the clamping screw on the fixed clamp. Trim any excess sample.
9. Position the thermocouple so that it is approximately halfway between the two clamps and close to, but not touching, the sample.
10. Place the thermal shield over the clamps, if you are using a heating rate of 2 °C/min or higher.



**Note: Do not use the thermal shield when using heating rates less than 2 °C/min or when performing a step and hold experiment.**

### 3.3.4.2 Running an Experiment

1. Open the TA Instrument Explorer Software for the Q800 DMA.
2. Set up the experimental parameters in the Summary Tab as follows:
  - a. Mode: **DMA Controlled Force**
  - b. Test: Custom
  - c. Enter the sample width and thickness into the appropriate boxes. The length should already be entered from using the **MEASURE** button when the sample was loaded. If not, use the sample length indicated on the touch screen in the Control Menu.
  - d. Indicate the sample name and any comments that should be made in the appropriate boxes.
  - e. Name the data file to your choosing and then click the **APPLY** button.

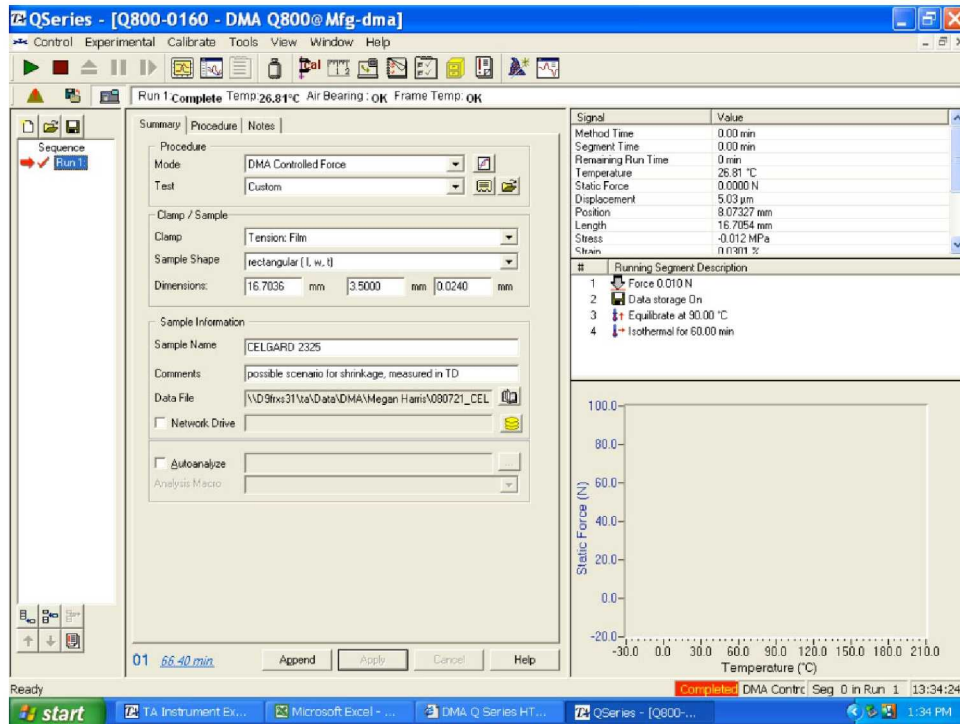


Figure 13.—Screen shot of correct Summary Tab.

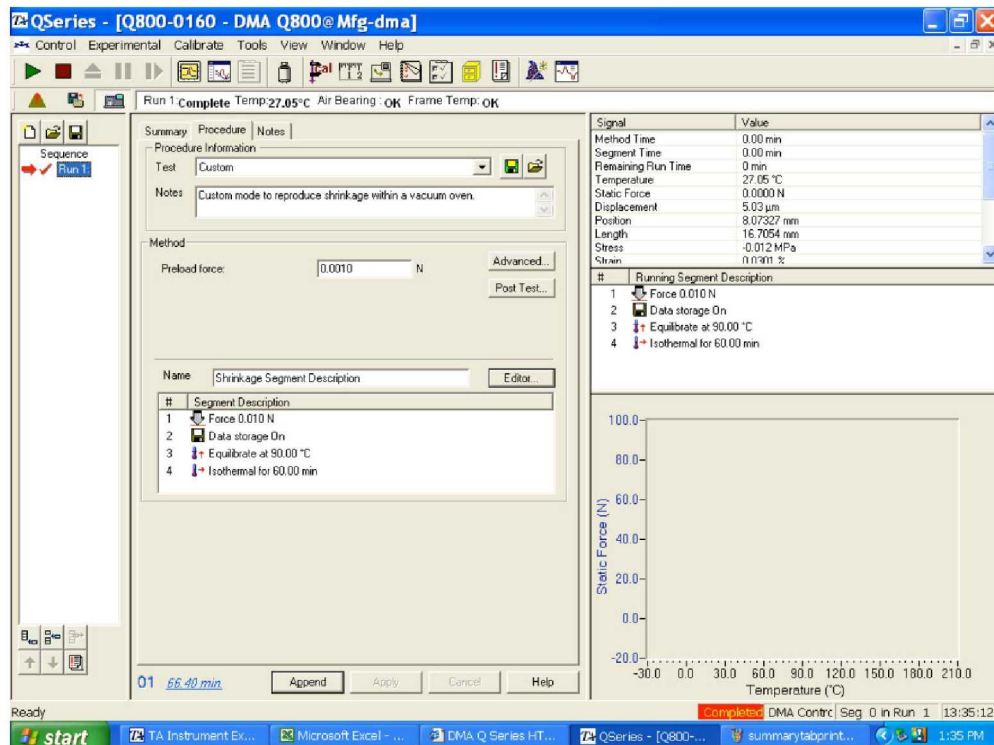


Figure 14.—Screen shot of correct Procedure Tab.

3. Set up the experimental parameters in the Procedure tab as follows:
  - a. Test: Custom
  - b. Preload Force: 0.001 N
  - c. Create and save a Running Segment Description using the Editor button as follows:

- (1) Force 0.010 N
- (2) Data storage: On
- (3) Equilibrate at 90.00°C
- (4) Isothermal for 60.00 min
- (5) End of method
- d. Enter any notes or commentary into the boxes provided in the Notes tab.
- e. Ensure that the sample is properly loaded into the film tension clamp and that all required measurements have been made and are accurate.
- f. Hit the APPLY button.
4. Press the **FURNACE** button to close the furnace.
5. Press the Green triangle in the upper left hand corner to start the run.
6. Once the run is complete, allow the clamp, furnace, and sample to completely cool down before removing the sample from the clamp.
7. Loosen the two clamping screws and open the clamp faces and remove the sample.
8. Use a knife or razor blade to gently scrape all clamp faces to remove any residue. Be careful not to scratch the clamp faces.

### 3.3.5 Analysis and Results

1. Open the Universal Analysis Software and open the filename of the sample just run.
2. Click on the **SIGNALS** button in the top right hand corner of the pop up screen that comes up.
3. For the Y1 axis, select “Displacement” as the signal. For all other Y-axes, ensure that the boxes appear as “Not Used”. For the x-axis, select “time”, then hit **OK**. Hit **OK** one more time and the graph should appear.
4. Right click in the center of the graph and select “Curve Value at X” which will be towards the bottom.
5. Move the red line to the end of the graph right before the data ends, which will indicate maximum displacement. Right click again and hit “Accept Limits”. Ensure that you label the point with “Signal: Displacement”. The value that appears will be the displacement of the separator sample.
6. To calculate shrinkage, you must also know the original length of the sample before testing was performed. This value can easily be obtained by clicking the **VIEW** button and then selecting “Parameter Block”. The length will be the first number after the word “Size”.
7. Open the calculator on the computer or find a hand held calculator to do the following calculation: Take the displacement value (which is in units of micrometers) and move the decimal place to the left three places. This will make displacement in units of millimeters. Divide this new displacement value (in units of millimeters) by the original length (which is in units of millimeters) and then multiply by 100. The value that appears will be percent shrinkage for that particular separator sample
8. Repeat this procedure as many times as needed for an accurate analysis of the data.

This procedure produced consistent and comparable results with both baseline Celgard and Tonen separators. It is easily reproducible and a much more precise indicator of shrinkage that wastes little separator material

Sample: TONEN  
 Size: 18.6600 x 3.0000 x 0.1200 mm  
 Method: Constant Temperature at 90  
 Comment: possible scenario for shrinkage, measuring in direction A

DMA

File: C:\...DMA\Megan Harris\080714\_TONEN.002  
 Run Date: 14-Jul-2008 11:20  
 Instrument: DMA Q800 V7.5 Build 127

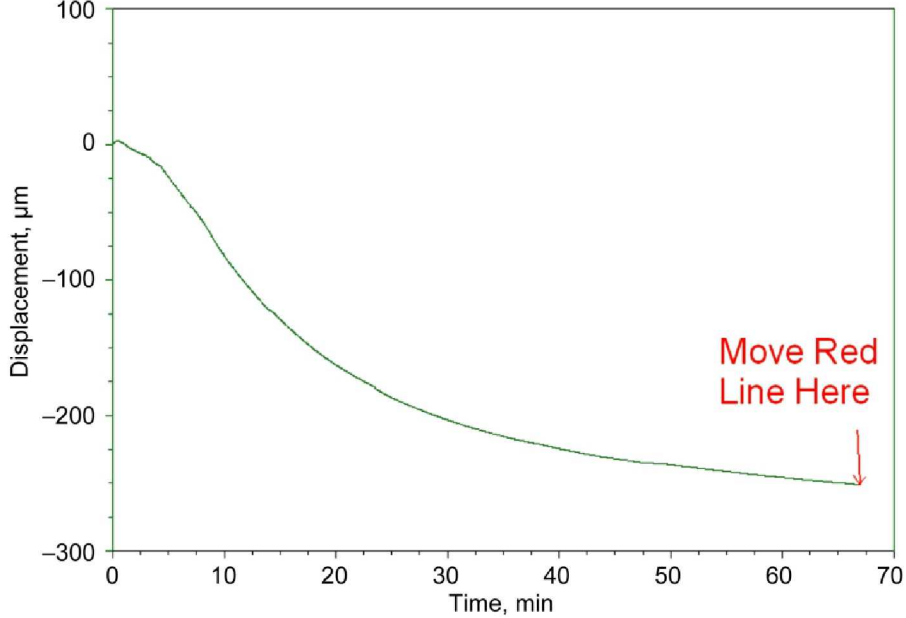


Figure 15.—Method of finding displacement.

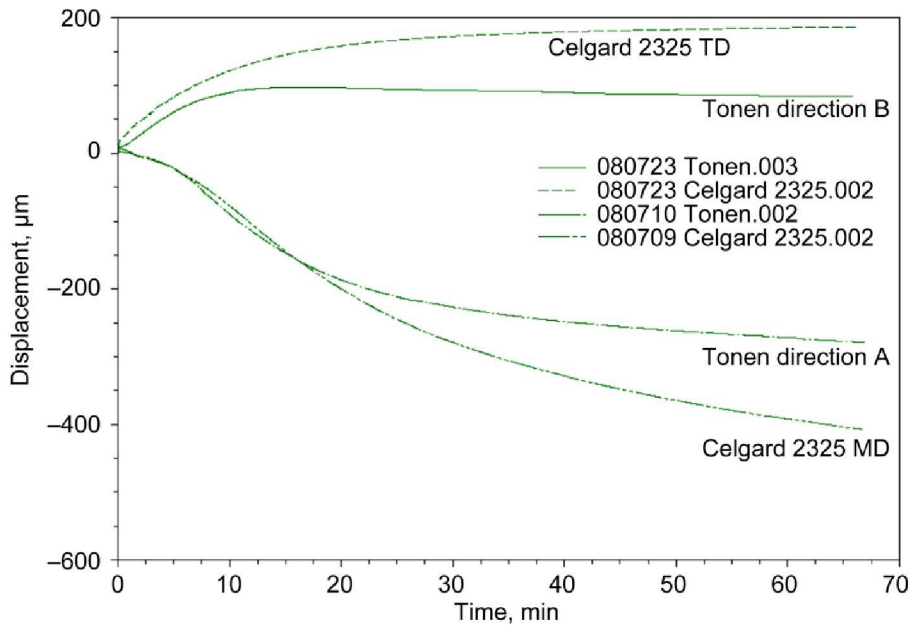


Figure 16.—Displacement versus time for Celgard 2325 and Tonen in both directions.

### 3.4 Tensile Strength

#### 3.4.1 Purpose

The separator is often wound with the electrodes under tension during cell fabrication. The separator must not elongate significantly under the tension, else the width would change. A tensile strength specification is sometimes given, but the key parameter is Young's modulus in the machine direction. As

Young's modulus is difficult to measure, the 2% offset yield is a good measure; less than 2% offset at 1000 psi is acceptable for many winding machines.

### 3.4.2 Scope

Techniques for measuring the tensile strength of separators are described. The methods utilize a film tension clamp on a Dynamic Mechanical Analyzer (DMA) and a strain ramp.

A separator should be strong enough to withstand mechanical handling during cell winding and assembly. It should be dimensionally stable and should not neck down during winding. A decrease in width will allow the electrodes to touch each other and create a short. Thus the tensile property of the separator should be very strong in the MD (machine direction) compared to the TD (transverse direction). Since the DMA can only measure tensile strength in one dimension, this test must be run in both the machine direction (MD) and transverse direction (TD).

The procedures presented in this document can give the experimenter the following tensile strength indicators:

1. Young's Modulus
2. Strain at Break
3. Displacement at Break
4. Stress at Break

### 3.4.3 Equipment

#### 3.4.3.1 TA Instrument's Q800 DMA

The Q800 DMA instrument description is identical to that included in Section 3.3.

To measure tensile strength the film tension clamp will be utilized. Conditions will be held isothermal around room temperature while strain is ramped until the separator sample breaks or loses its mechanical integrity or until the drive shaft on the DMA cannot travel any further.

#### 3.4.3.2 Separator Sample

A rectangular separator sample can easily be cut with a razor blade in either direction. Ensure that the sample is between 3- to 4-mm wide and around 10- to 12-mm long and has straight edges. Remember that this test must be performed in both MD and TD to determine tensile strength in both directions.

**Note: If the sample does not break after numerous tests but rather stretches out, the sample length should be minimized to ensure the maximum possibility for sample breakage.**

**Note: Gloves should be worn at all times when handling the DMA or separator samples to ensure no contamination or degradation of the machine or clamp occurs.**

### 3.4.4 Procedure

**Note: Before beginning the procedure, ensure that the film tension clamp has been properly installed and calibrated. Also ensure that other calibrations (instrument, position, temperature) have been performed. For details, see the TA Instrument's Q800 DMA Calibration Manual.**

#### 3.4.4.1 Loading the Sample

After the film tension clamp has been installed on the DMA, you can mount the sample using the steps found in Section 3.3.4.1.

#### 3.4.4.2 Running an Experiment

1. Open the TA Instrument Explorer Software for the Q800 DMA.
2. Set up the experimental parameters in the Summary tab as follows:
  - a. Mode: DMA Strain Rate

- b. Test: Strain Ramp
- c. Enter the sample width and thickness into the appropriate boxes. The length should already be entered from using the **MEASURE** button when the sample was loaded. If not, use the sample length indicated on the touch screen in the Control Menu.
- d. Indicate the sample name and any comments that should be made in the appropriate boxes.
- e. Name the data file to your choosing and then click the **APPLY** button.

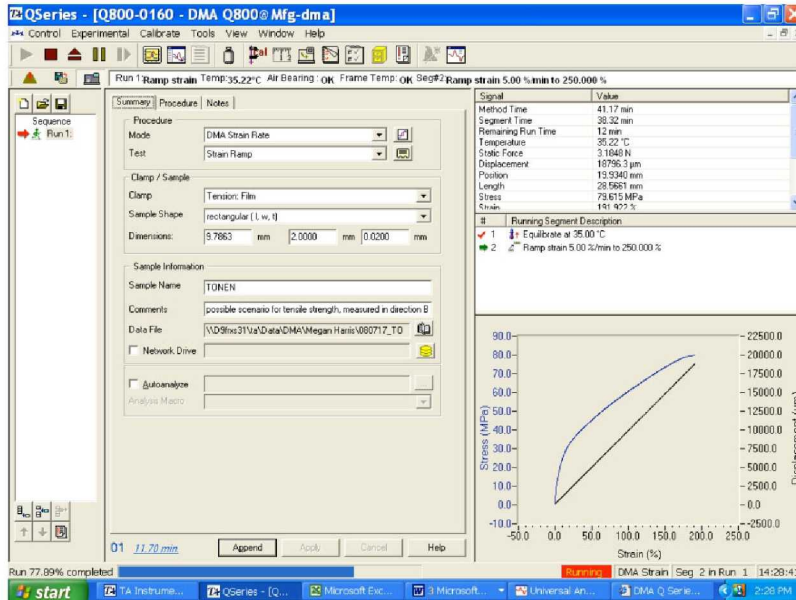


Figure 17.—Screen shot of correct Summary Tab.

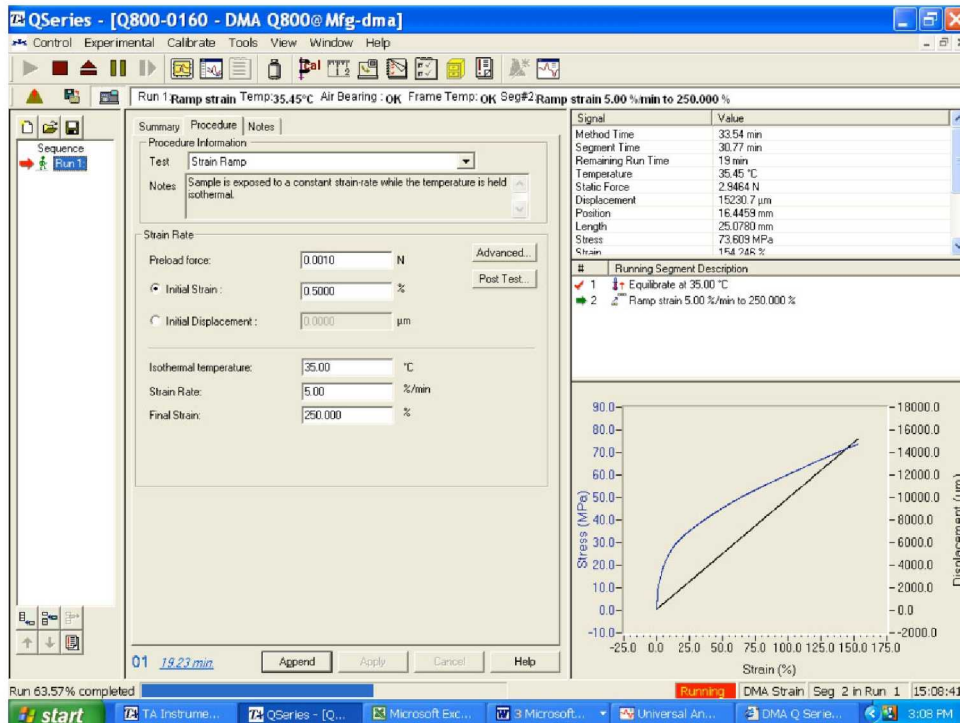


Figure 18.—Screen shot of correct Procedure Tab.

3. Set up the experimental parameters in the Procedure tab as follows:
  - a. Test: Strain Ramp
  - b. Preload Force: 0.001 N
  - c. Initial Strain: 0.5%
  - d. Isothermal Temperature: 35 °C
  - e. Final Strain: 250%
  - f. Ramp rate: 5%/min
  - g. Enter any notes or commentary into the boxes provided in the Notes tab.
  - h. Ensure that the sample is properly loaded into the film tension clamp and that all required measurements have been made and are accurate.
  - i. Hit the **APPLY** button.
4. Press the **FURNACE** button to close the furnace.
5. Press the Green Triangle in the top left hand corner to start the run
6. Once the run is complete, allow the clamp, furnace, and sample to completely cool down before removing the sample from the clamp.
7. Loosen the two clamping screws and open the clamp faces and remove the sample.
8. Use a knife or razor blade to gently scrape all clamp faces to remove any residue. Be careful not to scratch the clamp faces.

### 3.4.5 Analysis and Results

1. Open the Universal Analysis Software and open the filename of the sample just run.
2. Click on the **SIGNALS** button in the top right hand corner of the pop up screen that comes up.
3. For the Y1 axis, select “Stress” as the signal. For the Y2 axis, select “Displacement” as the signal. For all other Y-axes, ensure that the boxes appear as “Not Used”. For the X-axis, select “Signal” and then select “Strain”, then hit **OK**. Hit **OK** one more time and the graph should appear.
4. To determine displacement at break (in units of  $\mu\text{m}$ ) right click on the displacement line right where the data ends and displacement is at a maximum. A screen should appear which will show the value of displacement. Select the number that is in micrometer ( $\mu\text{m}$ ) units and the result should be displayed on the graph. This value is displacement at break.
5. To determine stress at break, find the value in the curve where stress is at a maximum and then it begins to decline. Right click on this point on the curve and a screen should appear which will show the value of stress at break. Select the number that is in units of MPa and the result should be displayed on the graph. This value is stress at break.
6. To determine strain at break, right click on either the same point where you found displacement at break or stress at break. A screen should appear which will show the value of strain. Select the number that is listed as a percentage and the result should be displayed in the graph. This value is strain at break.
7. To determine Young’s modulus, you must find the slope of the linear portion of the stress vs. strain graph. To do this, right click in the middle of the graph and select “Signals” which should be towards the top. For the Y1 axis, select “Stress” and for all other Y-axes, ensure that the boxes appear as “Not Used”. For the X-axis, select “Signal” and then select “Strain”, then hit **OK**. To find the slope of the linear portion of this graph, right click in the middle of the graph and select “Slope” which will be towards the bottom. Move the two red lines to the boundaries of the line you want to use. Once the red lines are in the appropriate places, right click again and select “Accept Limits”. The slope of the portion of the graph you selected should be displayed on the graph and this value is Young’s modulus.

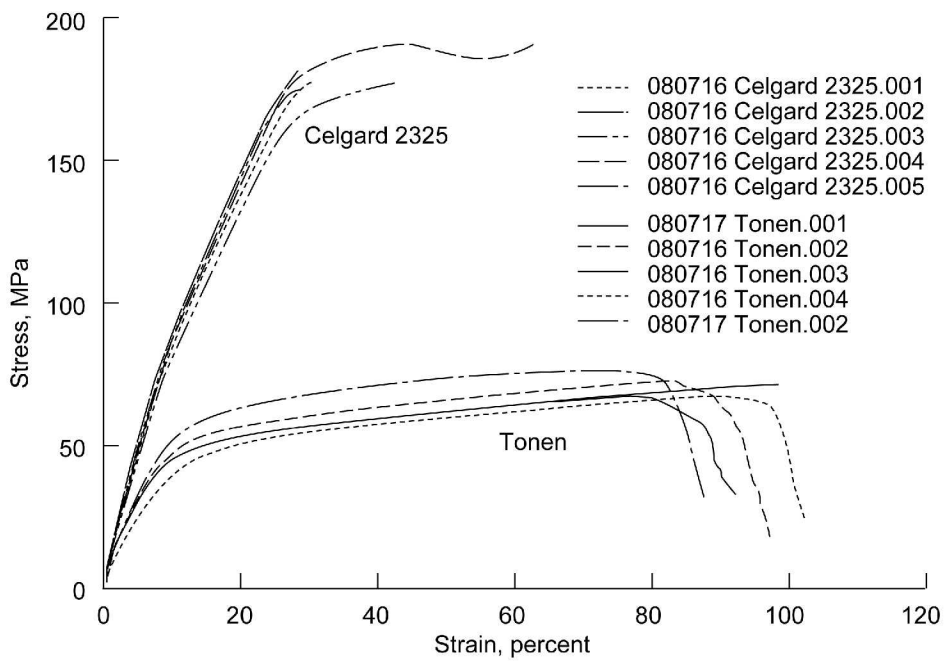


Figure 19.—Stress versus strain curve for Celgard 2325 in MD and Tonen in direction A.

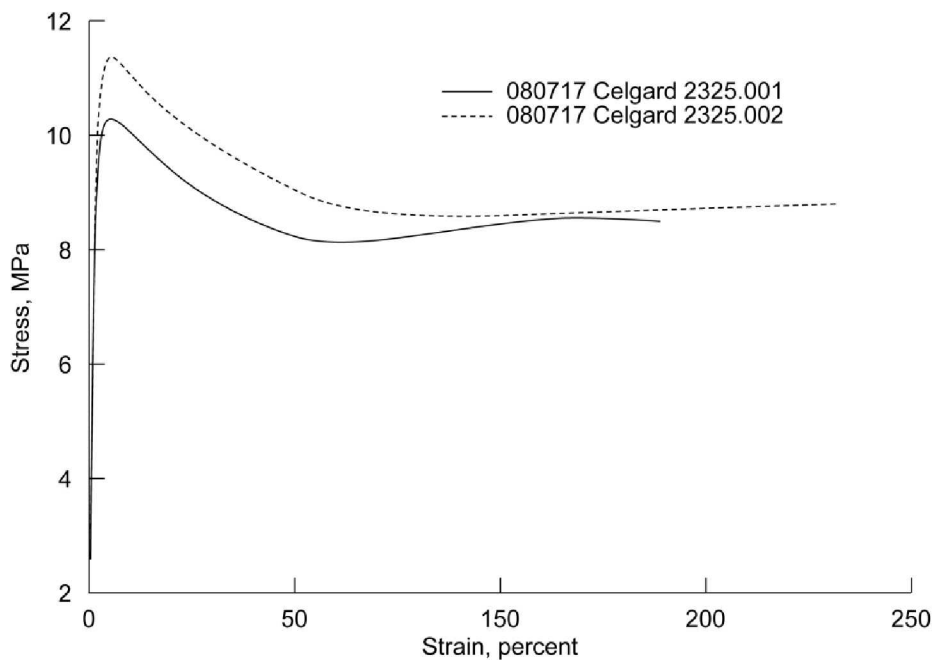


Figure 20.—Stress versus strain curve for Celgard 2325 in TD. These samples never actually broke.



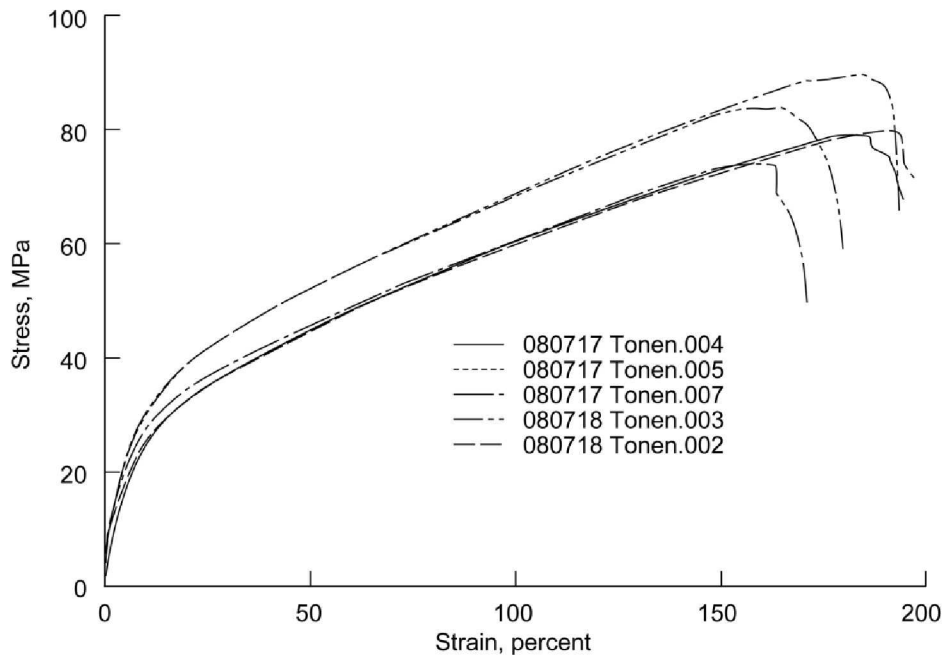


Figure 21.—Stress versus strain curve of Tonen in direction B.

This procedure did produce consistent results which were similar to values reported from the manufacturers. However, since specific parameters and specifications were not reported from Celgard LLC and Tonen, parameters were chosen which resulted in quantitative differences from the manufacturer’s literature.

### 3.5 Melt Integrity

#### 3.5.1 Purpose

This procedure documents methods for measuring the melt integrity of separators. Melt integrity is a critical property that affects the mechanical and electrical properties of a battery. Separators with good mechanical integrity at high temperatures can provide a greater margin of safety for lithium-ion cells by preventing the electrodes from contacting one another. The temperature at which the separator loses physical integrity (viscosity becomes low enough to allow the electrodes to contact) can be identified by measuring the elongation of a separator film under load (~5 g/cm) as a function of temperature.

#### 3.5.2 Scope

Techniques for measuring the melt integrity of separator materials are described. The methods are based on Thermal Mechanical Analysis (TMA). Utilizing TMA with a Dynamic Mechanical Analyzer (DMA), the separator is held under a constant load/stress with a temperature ramp and the degree of elongation or displacement is measured. The temperature at which the elongation increases dramatically is when the separator loses its mechanical integrity and thus its safety factor.

Typically, separators show some shrinkage and then start to elongate and then finally break. This test utilizes a small separator sample (about 10 mm length (MD) and about 3 mm width (TD)) which is held in the film tension clamp. The sample is held with a constant 0.02 N load while the temperature is ramped at 5 °C/min past the melting point of the material until the tension ruptures the film. Three parameters are reported from the procedure:

1. Shrinkage onset temperature
2. Deformation temperature
3. Rupture temperature

Separators with a rupture temperature greater than 150 °C are desirable for lithium-ion cells.

### 3.5.3 Equipment

#### 3.5.3.1 TA Instrument's Q800 DMA

The Q800 DMA instrument description is identical to that included in Section 3.3.

To measure melt integrity utilizing TMA, a film tension clamp will be used. A constant stress will be applied while ramping temperature on the sample and elongation/displacement will be measured and recorded.

#### 3.5.3.2 Separator Sample

A rectangular separator sample can easily be cut with a razor blade in the MD. Ensure that the sample is between 3 to 4 mm wide and around 10 to 12 mm long and has straight edges.

### 3.5.4 Procedure

**Note: Before beginning the procedure, ensure that the film tension clamp has been properly installed and calibrated. Also ensure that other calibrations (instrument, position, temperature) have been performed. For details, see the TA Instrument's Q800 DMA Calibration Manual.**

#### 3.5.4.1 Loading the Sample

After the film tension clamp has been installed on the DMA, you can mount the sample using the steps found in Section 3.3.4.1.

#### 3.5.4.2 Running an Experiment

1. Open the TA Instrument Explorer Software for the Q800 DMA.
2. Set up the experimental parameters in the Summary Tab as follows:
  - a. Mode: DMA Controlled Force
  - b. Test: Temp Ramp/Controlled Force
  - c. Enter the sample width and thickness into the appropriate boxes. The length should already be entered from using the **MEASURE** button when the sample was loaded. If not, use the sample length indicated on the touch screen in the Control Menu.
  - d. Indicate the sample name and any comments that should be made in the appropriate boxes.
  - e. Name the data file to your choosing and then click the **APPLY** button.
3. Set up the experimental parameters in the Procedure tab as follows:
  - a. Test: Temp Ramp/Controlled Force
  - b. Preload Force: 0.02 N
  - c. Start Temperature: 30°C
  - d. Final Temperature: 200°C
  - e. Ramp rate: 5°C/min
  - f. Enter any notes or commentary into the boxes provided in the Notes tab.
  - g. Ensure that the sample is properly loaded into the film tension clamp and that all required measurements have been made and are accurate.
  - h. Hit the **APPLY** button

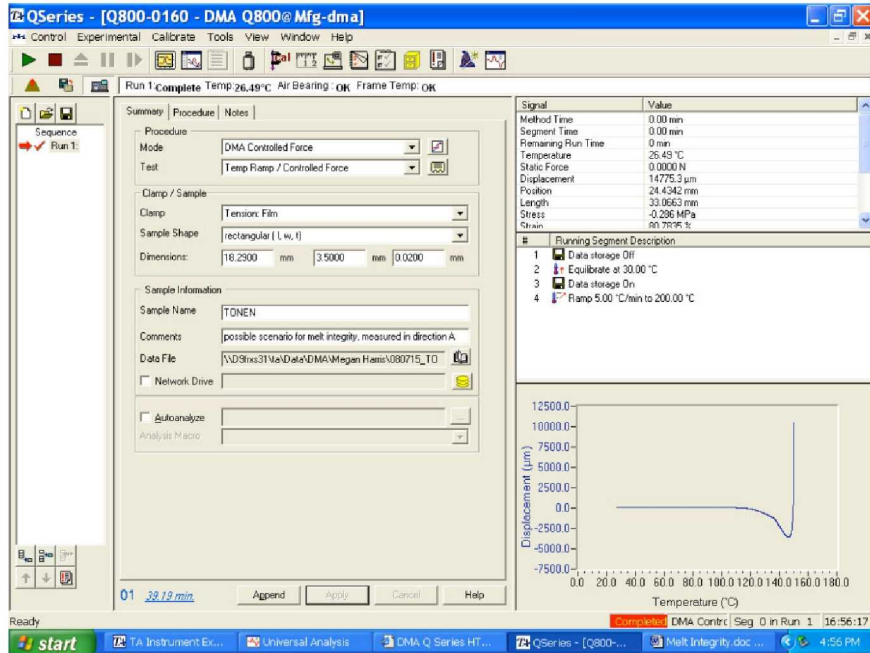


Figure 22.—Screen shot of correct Summary Tab.

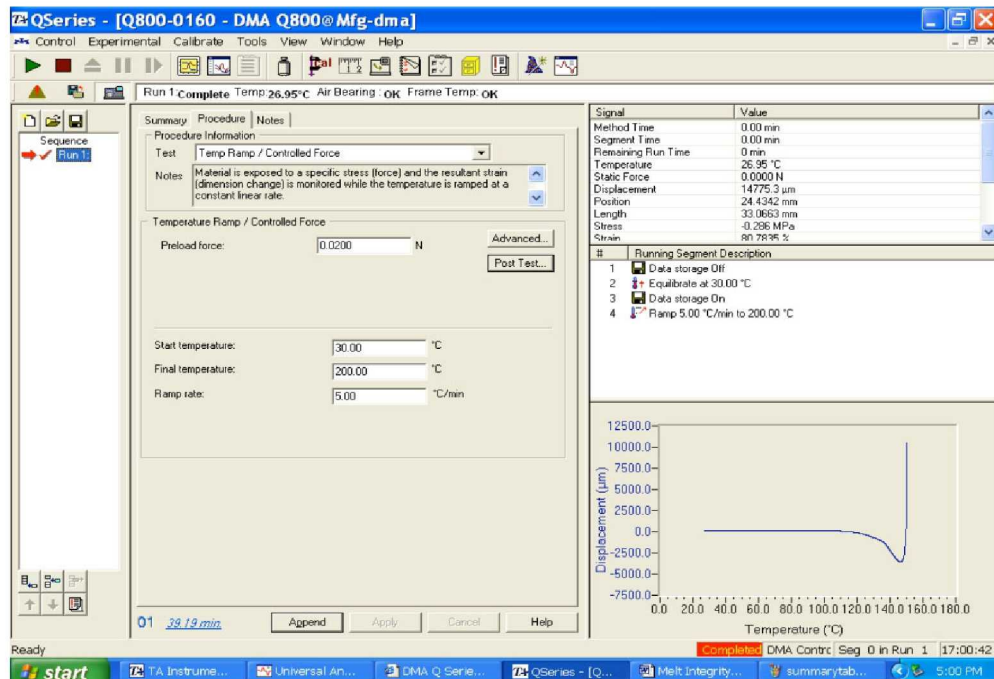


Figure 23.—Screen shot of correct Procedure Tab.

4. Press the **FURNACE** button to close the furnace.
5. Press the Green Triangle in the top left hand corner to start the run.
6. Once the run is complete, allow the clamp, furnace, and sample to completely cool down before removing the sample from the clamp.
7. Loosen the two clamping screws and open the clamp faces and remove the sample.

- Use a knife or razor blade to gently scrape all clamp faces to remove any residue. Be careful not to scratch the clamp faces.

### 3.5.5 Analysis and Results

- Open the Universal Analysis Software and open the filename of the sample just run.
- Click on the **SIGNALS** button in the top right hand corner of the pop up screen that comes up.
- For the Y1 axis, select “Displacement” as the signal. For all other Y-axes, ensure that the boxes appear as “Not Used”. For the X-axis select “Temperature”, and then hit **OK**. Hit **OK** one more time and the graph should appear.
- To determine shrinkage onset temperature, right click on the area of the curve where displacement begins to decrease. A screen should appear which will show the value of shrinkage onset temperature. Select the number that is in units of °C and the result should be displayed on the graph. This value is shrinkage onset temperature.
- To determine deformation temperature(s), right click on the area/s of the curve where a sort of “hump” occurs. For a more clear illustration, see the figure below. A screen should appear which will show the value of deformation temperature. Select the number that is in units of °C and the result should be displayed on the graph. This value is deformation temperature. Note: Some separators will have only one deformation temperature while others will have multiple deformation temperatures. It is at the discretion of the experimenter to decide what is an actual deformation temperature versus just a discrepancy in the data.
- To determine rupture temperature, right click on the area of the curve where displacement begins to increase dramatically and an indication of separator rupture is obvious. For a more clear illustration, see the figure below. A screen should appear which will show the value of rupture temperature. Select the number that is in units of °C and the result should be displayed on the graph. This value is rupture temperature.
- Repeat this procedure as many times a needed for an accurate analysis of the data.

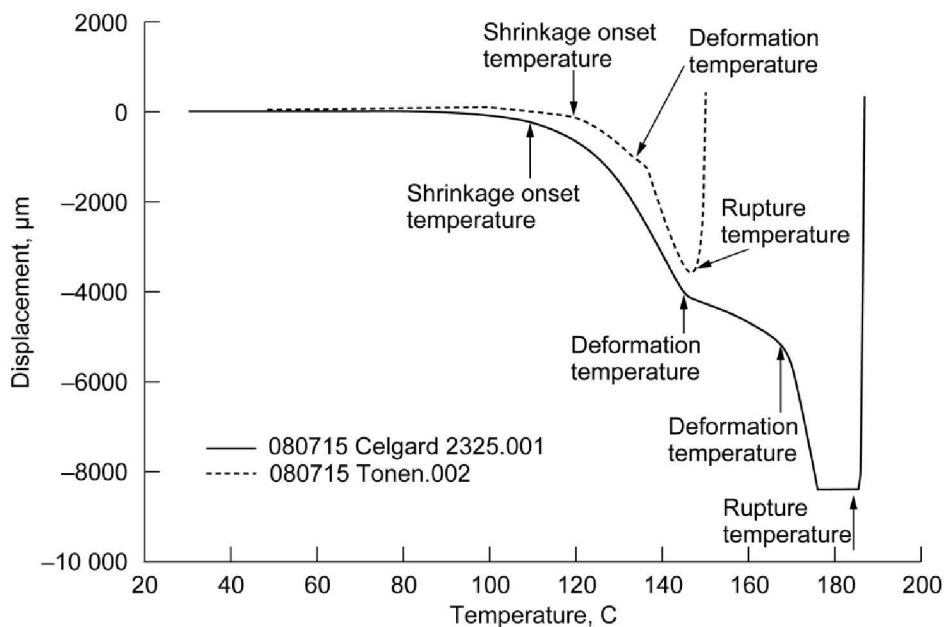


Figure 24.—Illustration of various temperature regimes.

Separator	Celgard 2325 (PP-PE-PP)	Tonen (PE)
Shrinkage onset temperature	119.1 °C	126.9 °C
Deformation temperature(s)	145.2 °C , 170.3 °C	139.3 °C
Rupture temperature	180.7 °C	150.2 °C

Figure 25.—Experimental mean values obtained for baseline separators.

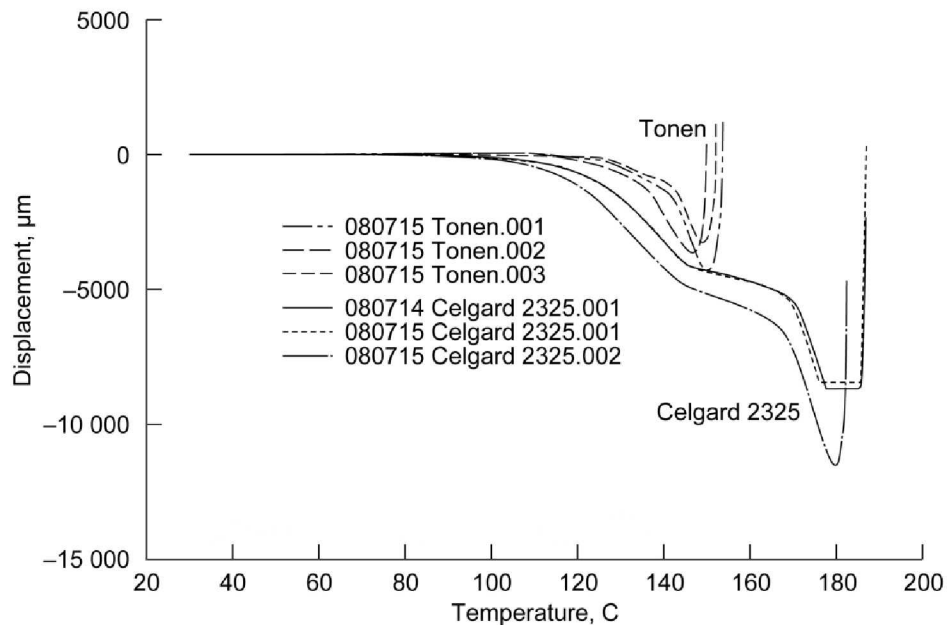


Figure 26.—Melt integrity results for Celgard 2325 and Tonen baseline separators.

### 3.6 Mix Penetration Strength

#### 3.6.1 Purpose

During the winding of the spiral wrap construction, considerable mechanical pressure is applied to the cathode-separator-anode interface. Any loose particle could be forced through the separator and short-circuit the cell. This procedure documents a method for measuring the “mix penetration strength” of a lithium-ion battery separator, which represents a measure of the susceptibility to particle penetration. Mix penetration strength is a critical property that ultimately affects when a battery may short-circuit and possibly proceed into a thermal runaway condition.

#### 3.6.2 Scope

The following method is based on a “ball crush test” to simulate conditions within an actual battery instead of the separator standing alone. Within this procedure, the separator is placed between a cathode and anode strip to simulate the orientation within a battery. Two force plates are brought together with a steel ball in between and the force is measured at the point at which a short-circuit occurs. The measured force is the “mix penetration strength” as it is a measure of the penetration of the mix of cathode and anode into the separator (Ref. 9).

The mix penetration strength should be at least 100 kgf/mil for separators used in lithium-ion cells. Illustrations are specific to a Carver Hydraulic Press.

### 3.6.3 Equipment

#### 3.6.3.1 Carver Automatic Hydraulic Press

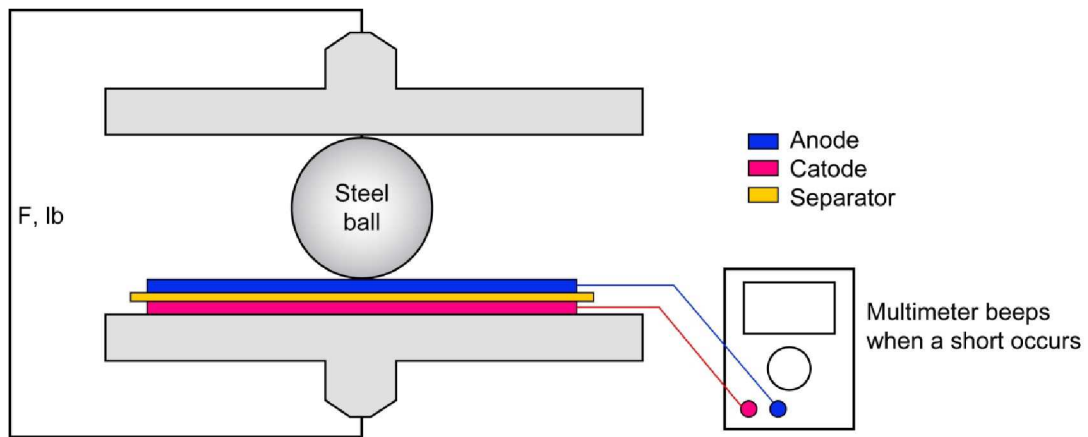


Figure 27.—Basic schematic of mix penetration strength apparatus.



Figure 28.—Carver automatic hydraulic press.

### 3.6.3.2 Adjusting Press Settings in Automatic Mode

**Note: Ensure that the operator has read all safety warnings and information and is properly trained to use the Carver Hydraulic Press before turning on and running the press.**

1. Turn on the press using the POWER switch. If the display does not appear, look on the right side of the machine and ensure that the red knob is facing the number 1 and then try again.
2. Depress the [AUTO] key.
3. Depress the [MENU] key. The VIEW/EDIT RECIPE submenu will appear.
4. Depress the [SET] key once to reveal the FORCE parameter (pounds/tons/kilograms)
5. Use the [ARROW UP] key to increase or the [ARROW DOWN] key to decrease the force set point. Make the force set point significantly higher than the mix penetration strength value expected for a particular separator to ensure a short will occur.
6. Depress the [SET] key again to reveal the PUMP SPEED parameter. Use the [ARROW DOWN] key to set this to the lowest point (15 %).
7. Depress the [SET] key again to reveal the TIME BASE parameter where 0=sec and 1=min. Use the [ARROW UP] or [ARROW DOWN] key to switch to the desired time base.
8. Depress the [SET] key once more to reveal the DWELL TIME parameter. Set the Dwell Time to 0 (min or sec) using the [ARROW DOWN] key.
9. The press is now ready to be used for a test.

### 3.6.3.3 Plate With Steel Ball

#### 3.6.3.3.1 Multimeter

A FLUKE 73 III Multimeter is used to indicate a short circuit while the force is increased on the separator “sandwich”. It has a mode that allows the multimeter to beep when a short circuit occurs. The leads from the multimeter can easily be attached to the foils on the anode and cathode with alligator clips.

### 3.6.4 Procedure

#### 3.6.4.1 Sample Preparation and Mounting

1. Cut a piece of anode and cathode so that they are rectangular in shape and roughly the same size. This test is a lot easier to run if the anode and cathode have outward foils on them which allow for easy clipping with the alligator clips on the multimeter leads.
2. Cut a piece of separator so that it is rectangular as well and is slightly larger than the anode and cathode strips to ensure that a short will not occur by accident.
3. Place the separator sample between the anode and cathode strips and use Kapton tape to secure the sandwich together. Ensure that the anode and cathode are touching the separator properly in all places.
4. Place a few thick metal plates on the bottom platen in the carver press to take up space between the two platens. Place the steel ball plate on top of these plates so that the ball is facing upwards.
5. Tape the separator sandwich onto a thin piece of Bakelite that is the same dimensions as the steel ball plate, using double sided tape. Clamp this piece of Bakelite (with sandwich attached) onto the top platen using larger sized office clamps so that the sandwich is facing down towards the steel ball but not touching it.
6. Attach the leads from the multimeter onto the appropriate foils of the anode and cathode strip. The multimeter can sit just right outside of the door of the Carver Press.
7. Ensure that the steel ball will hit the sandwich in an appropriate place to allow a short to occur. This will most likely be in the center of the sandwich.
8. Once everything is properly in place and ready for testing, close the safety shield door on the press.

#### **3.6.4.2 Running a Test**

1. Ensure that the press has been programmed according to the directions in the Carver Press section of this document.
2. When the safety shield door is in the closed position, start the cycle by simultaneously depressing and holding both [CLOSE] pushbuttons until the press closes and begins to build pressure. (If either of the pushbuttons are released before pressure is built, the press will open.)
3. The press will build pressure until the clamp force set point is reached. When the press is building force, the LCD screen will display the current applied force. Watch this force while simultaneously listening for a beep from the multimeter indicating a short circuit. Record the force at which a beep occurs. Release the [CLOSE] pushbuttons once the test is complete

#### **3.6.4.3 Sample Teardown**

If the separator sandwich is large enough, the double sided tape can be removed and the sandwich moved to another location on the Bakelite sheet to allow for another location to be penetrated by the steel ball. However, ensure that there is plenty of clearance and that the new penetration site is far away enough from the site that was already penetrated.

#### **3.6.5 Analysis and Results**

A preliminary evaluation of this procedure was performed twice within the laboratory with a Celgard 2325 separator and a Carver press that was available in-house. Expected shorts did occur during both tests around 2500 lbf, however, the force reading increments for the specific Carver press employed were not precise enough for the measurements that were desired. Although somewhat time-consuming, this procedure, which employs actual cathode and anode materials, has the potential of more accurately simulating mechanical abuse conditions in an actual cell.



## **4.0 Thermal Performance Profile**

If a lithium-ion cell is accidentally overcharged or abused, heat can be generated that could seriously compromise cell and battery-level safety, which is especially critical for human-rated applications. Above a threshold temperature, a “self-heating” condition could occur due to exothermic reactions occurring internally within the cell. Such reactions may include reactions between lithium and electrolyte and the thermal decomposition of internal cell components. If the internal heat generation is allowed to continue, a catastrophic cell “thermal runaway” condition could occur, which would be a serious safety concern for a manned application.

For battery (and human-rated) safety, it is desirable for a state-of-the-art battery separator utilized with lithium-based cell chemistries to possess an inherent ability to shut the battery down (i.e., terminate the flow of electric current) if overheating, for example, occurs. Thus, screening methods for evaluating separator thermal properties, thermal stability and “shutdown” characteristics were formulated.

### **4.1 Differential Scanning Calorimetry (DSC)**

#### **4.1.1 Purpose**

This procedure documents methods for measuring separator thermal transitions. Thermal transitions such as glass transition, crystallization and melting are critical properties that enable determination of melt integrity, mechanical robustness and shutdown temperature of separators. Melt integrity, mechanical robustness, and shutdown temperature influence separator performance because low melt integrity, mechanical weakness and a nonexistent shutdown temperature are unwanted characteristics. Accurate measures provide a valuable screening tool for candidate separator materials.

#### **4.1.2 Scope**

Techniques for measuring the thermal transitions of lithium-ion battery separators are described. The methods are based on differential scanning calorimetry (DSC). A simple, thermo-analytical method for interpreting the graphical representation of the thermal transitions is presented. DSC theory and more advanced interpretation techniques are beyond the scope of this procedure.

The procedure heats two pans at the same rate. One pan contains a sample and the other is the reference pan. The heater underneath the sample pan has to work harder than the reference pan heater. How much more heat is used by the sample pan to keep heating at the same rate is what is measured. It is essential that the specimen has a specific weight to allow for proper comparison.

It is preferable that lithium-ion battery separator samples be tested as freestanding films (i.e., not bonded to a substrate or carrier).

#### **4.1.3 Equipment**

A TA Instruments Model 2910 Differential Scanning Calorimeter (DSC) is employed for the thermal analysis, and the user should refer to the operating manual for the instrument.

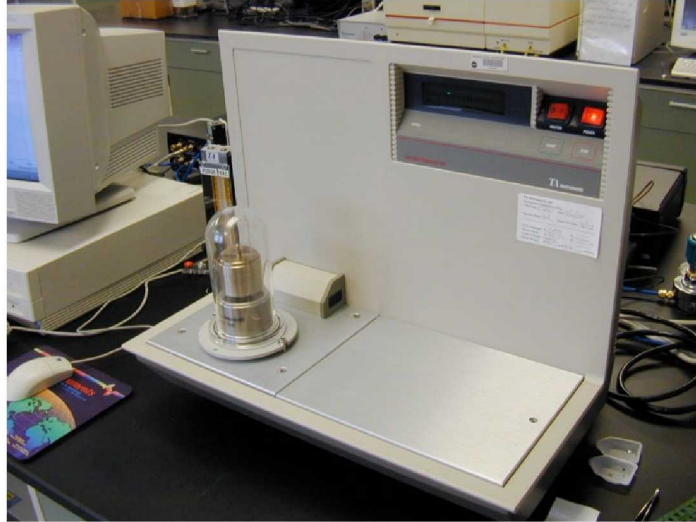


Figure 29.—TA instruments DSC.

#### 4.1.4 Procedure

1. Fold a piece of sample into 16 layers and punch out a 3/16 in. disk. Sample should weigh 3 to 5 mg depending on sample.
2. Weigh a set of the aluminum pan and lid accurately to  $\pm 0.02$  mg and record the weight.
3. Place a sample disk into the pan and weigh the set with the sample accurately to  $\pm 0.02$  mg. Record the weight and calculate the sample weight.
4. Crimp the pan and the lid together.
5. Reweigh the crimped pan. The weight should be the same before and after crimping. If not, remove the sample from the pan and start from step 2 again.
6. Prepare another set of pan and lid of about the same weight as the sample pan for reference.
7. Crimp the reference pan and lid together.
8. Turn on and operate DSC (TA Instruments 2910) according to the instrument operation manual.
9. Turn on the refrigerated cooling system and allow  $\frac{1}{2}$  hr to cool down before starting the test.
10. Place the sample and reference pan in the DSC cell.
11. Set up procedure as follows for polyethylene and/or polypropylene separators. For higher melting sample, change the final temperature from 200 to 30 °C higher than the melting temperature of the material:
  - a. Select Gas 1
  - b. Equilibrate at 30 °C
  - c. Ramp 5 °C/min to 200 °C
12. Start the run.
13. After the run is completed, start the Universal Analysis program, open the data file to display the thermal profile.
14. Record the melting temperature.

#### 4.1.5 Analysis and Results

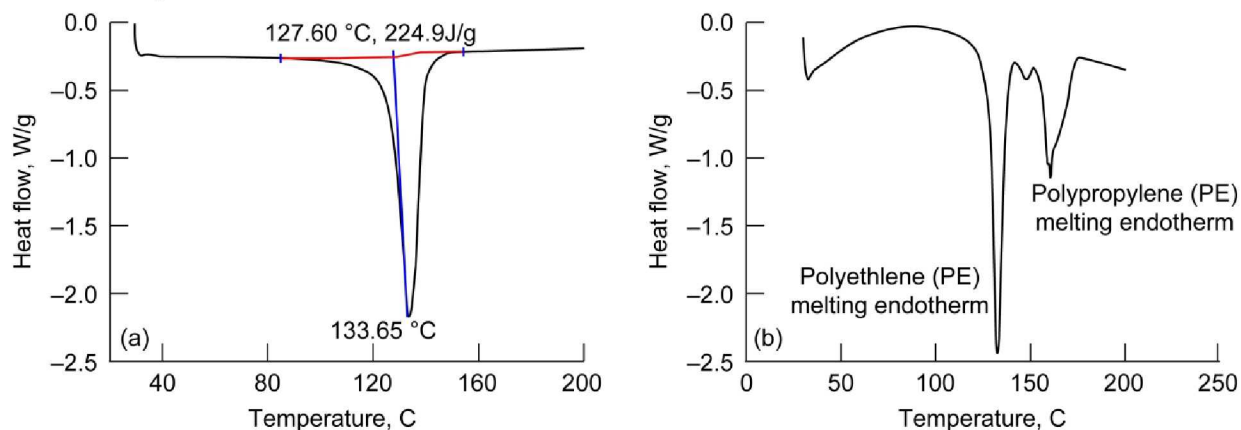


Figure 30.—DSC scans for (a) Tonen and (b) Celgard 2325 shutdown separator materials.

## 4.2 High-Temperature Cell Performance Integrity

Separators provide some margin of protection against short-circuit and overcharge in lithium-ion cells. With respect to this attribute, the separator material should also possess high-temperature **melt integrity** and exhibit mechanical robustness above a “shutdown” temperature, if such a mechanism for terminating the cell’s current flow exists. After a separator shutdown occurrence, the cell temperature is likely to continue to increase. The separator must maintain mechanical integrity and high electrical impedance as a function of time at elevated temperatures in order to prevent the electrodes from making physical contact and creating the safety hazard of an internal short circuit (Ref. 10).

### 4.2.1 Purpose

This procedure, which documents a method to screen a separator material with respect to its cell “shutdown” characteristics and mechanical integrity at elevated temperatures. If the separator loses mechanical integrity, then the electrodes could come into direct contact, react chemically, and result in thermal runaway.

### 4.2.2 Scope

If a separator material exhibits a large (1000X) increase in impedance at a target temperature, the ionic transport between the electrodes should effectively be terminated. The greater the mechanical integrity of the separator above the target temperature, the greater the margin of safety the separator can provide.

This procedure is an extension of Section 2.1, which screens a separator material with respect to ionic conductivity.

### 4.2.3 Equipment

A coin cell configuration is employed as a conductivity/resistivity cell and a Tenny environmental chamber is used for temperature control. For the impedance measurements, data was collect with an Arbin Instruments battery cycler with MITS PRO software, which could be programmed to perform basic electrochemistry procedures. Solartron 1250/1286 instruments, operated in conjunction with Scribner Zplot software, could also be used for the impedance measurements, if desired.

#### 4.2.4 Procedure

The ionic resistance of an electrolyte-flooded separator sample is monitored as the temperature is ramped, up to a point when the ionic current flow in an actual working full cell would be blocked. Cell resistance/impedance monitoring or electrochemical impedance spectroscopy (EIS) can be utilized for resistivity/conductivity measurements of the coin cell containing the separator sample.

A coin cell configuration is fabricated with the separator sample, but with three modifications:

1. A Nylon-6 (Zytel) gasket is used to seal the two coin cell case halves, due to its higher temperature integrity, as compared to polypropylene.
2. If deemed necessary based upon the temperature range under investigation, an alternative electrolyte with improved thermal stability characteristics can be employed. An example, which is stable to over 200 °C, is 1 M TFSI [lithium trifluoromethanesulfonimide (HQ-115, 3M Co.)] in a 1:1 by volume solution of propylene carbonate and triethylene glycol dimethyl ether.
3. Metal sheet tabs are spot welded to the coin cell can faces and a commercial coin cell holder is not employed.

##### 4.2.4.1 Impedance Measurements

Following the operational procedures and test schedule for AC impedance measurements with an Arbin Instruments battery cycler, coin cell resistance measurements are initially made at ambient temperature and repeated to verify reproducibility and good electrical contact between components. Measurements are made rapidly by the Arbin at a fixed 1 kHz frequency, which would be representative for the electrolyte-separator component in the coin cell. Resistance data is accumulated as the Tenney environmental chamber is ramped in temperature at a heating rate of 3 °C per minute.

#### 4.2.5 Analysis and Results

Preliminary data plots of measured resistance with increasing temperature are shown in Figure 31 for a baseline Tonen separator and in Figure 32 for a Celgard 2325 trilayer shutdown separator. For the single layer Tonen sample, the resistance drastically increased after the melting temperature of the polyethylene separator material, but then started decreasing, possibly due to soft shorts beginning to occur. The runs were terminated at ~170 °C.

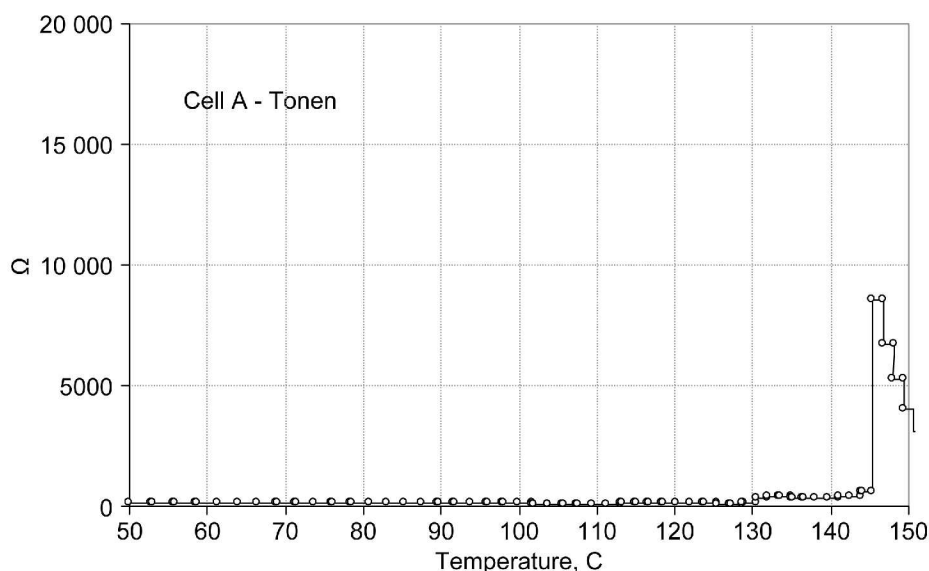


Figure 31.—Tonen separator high-temperature integrity data.

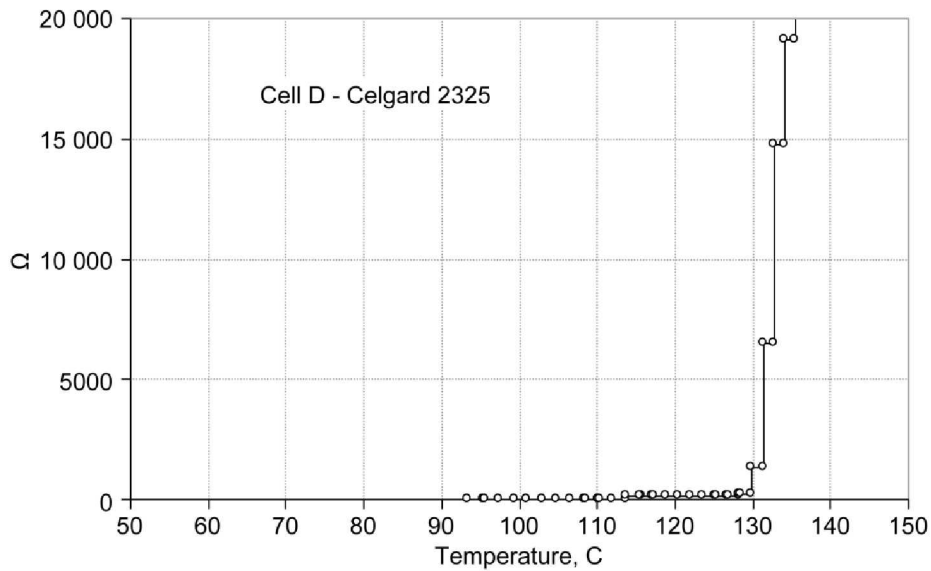


Figure 32.—Celgard 2325 separator high-temperature integrity data.

For the Celgard 2325 sample, which consists of a polyethylene layer sandwiched between two higher-melting polypropylene layers, the resistance continued to increase from the polyethylene layer melting point. A desired scenario in an actual working cell would be that this event would have closed the pores in the polyethylene layer and, thus, terminating the current flow, but mechanical integrity would have been preserved at this high temperature by the polyethylene layers, thus preventing an internal short-circuit.

## 5.0 Summary

In support of the NASA Exploration Technology Development Program’s Energy Storage Project goal of selecting the optimal cell separator material(s) for the advanced lithium-ion battery technology and chemistries under development to address future NASA mission requirements, laboratory characterization and screening procedures have been established to assess and compare separator material-level attributes and the performance features related to such. Pertinent quantitative results obtained for the baseline separator materials are summarized in Table 1. For the purpose of making comparisons between different separator materials, results are relative to the specific procedures performed as described; such results do not represent “material specifications”, per se.

TABLE 1.—SUMMARY OF RESULTS OBTAINED FOR THE  
BASELINE CELGARD AND TONEN SEPARATOR MATERIALS

Separator Characteristics	Baseline Separator Material	
	Celgard 2325 (PP-PE-PP)	Tonen (PE)
Thickness (μm)	25	20
Ionic Conductivity at 23°C (mS/cm)	-----	0.6
Puncture Strength (kgf)	0.742 ± 0.176	0.927 ± 0.068
Thermal Shrinkage (%)		
MD	2.41 ± 0.17	N/A
TD	+1.51 ± 0.17	N/A
Direction A	N/A	1.36 ± 0.05
Direction B	N/A	+0.48 ± 0.22
<i>Note: The + sign indicates an elongation rather than a shrinkage</i>		
Tensile Strength—Ultimate Strain (%)		
MD	38.6	N/A
TD	*	N/A
Direction A	N/A	85.9
Direction B	N/A	178.7
Tensile Strength—Ultimate Stress (MPa)		
MD	179.9	N/A
TD	*	N/A
Direction A	N/A	70.76
Direction B	N/A	80.25
Tensile Strength—Displacement at Break (μm)		
MD	6516	N/A
TD	*	N/A
Direction A	N/A	10402
Direction B	N/A	18591
Tensile Strength—Young’s Modulus (MPa)		
MD	548.8	N/A
TD	*	N/A
Direction A	N/A	429.0
Direction B	N/A	30.4
High-Temperature Cell Performance Integrity Temperature at Ohmic Resistance Increase	130 to 135°C	145°C
Melt Integrity—Shrinkage Onset Temperature	119.1 °C	126.9 °C
Melt Integrity—Deformation Temperature(s)	145.2 °C , 170.3 °C	139.3 °C
Melt Integrity—Rupture Temperature	180.7 °C	150.2 °C
Notes: The MD and TD could not be unequivocally determined for the Tonen source material.		
*During tensile strength testing, the Celgard 2325 never broke in the transverse direction (TD).		

To complement the procedures developed and described herein, three additional tests, which would utilize a full-cell coin cell configuration with active electrodes, could be performed for further separator material screening and comparison, if desired:

1. Cell discharge performance testing to evaluate the influence of the separator conductivity and porosity on discharge rate
2. A forced overcharge test with temperature vs. time monitoring
3. An external short-circuit test with temperature vs. time monitoring

For tests 2 and 3 above, any safety breaches could be visually observed and the separator could be examined (e.g., by SEM) following a post-test coin cell disassembly, such as Destructive Physical Analysis (DPA).

Although such screening tools for material-level comparisons and selection will be very beneficial, additional in-depth testing will be required as the development program matures before human-rated, flight-quality cells can be realized.

As the program matures, all selected candidate cell component materials will need to be integrated into prototype laboratory cells, and actual cell-level performance assessed with realistic cell configurations and under operational and environmental conditions that simulate mission requirements. In addition to electrical performance and cycle-life evaluations, extensive safety and abuse testing will be critical at the cell level, and such testing will be instituted at governmental or contractor facilities that are equipped and skilled in performing such hardware evaluations. Representative cell-level testing which the cell separator component attributes can influence include:

- Discharge performance as a function of rate and temperature
- “Nail” penetration and “crush” tests to simulate short-circuit scenarios
- Overcharge testing
- Thermal performance and abuse testing such as “heat-to-vent” tests and Accelerating Rate Calorimetry (ARC) testing

External mechanical abuse (e.g., “nail” penetration or crush) or an internal short-circuit could result in an abnormal increase in cell temperature, which could seriously compromise safety. If an undesirable cell overcharge condition occurs, dendritic lithium metal could form, which could penetrate the separator as well as causing a drastic reduction in thermal stability.

Following successful technology evaluation at the individual cell level, full battery-level configurations will have to be evaluated and qualified for integration into future flight hardware systems. For example, cell component attributes that enhance safety, such as a “shutdown” separator, at the cell level may have a negative impact on safety at the battery level under certain system design and operational conditions (Ref. 10).





## Appendix A.—Separator Sample Thickness Measurement Data Form

Date: \_\_\_\_\_

Experimenter: \_\_\_\_\_

Material ID: \_\_\_\_\_

### A.1 Physical Description

Color	_____
Clarity	_____
Tack	_____
Flaws	_____
	_____
	_____
	_____

### A.2 Sample Thickness Measurements

Perimeter (mm): _____	Minimum (mm): _____
	Maximum (mm): _____
Center (mm): _____	
Mean thickness (mm): _____	



## Appendix B.—Puncture Strength Data Form

Date: \_\_\_\_\_

Experimenter: \_\_\_\_\_

Material ID: \_\_\_\_\_

Sample 1 \_\_\_\_\_ kgf

Sample 2 \_\_\_\_\_ kgf

Sample 3 \_\_\_\_\_ kgf

Sample 4 \_\_\_\_\_ kgf

Sample 5 \_\_\_\_\_ kgf

Sample 6 \_\_\_\_\_ kgf

Sample 7 \_\_\_\_\_ kgf

*Mean Puncture Strength* \_\_\_\_\_ kgf



## Appendix C.—Thermal Shrinkage Data Form

Date: \_\_\_\_\_

Experimenter: \_\_\_\_\_

Material ID: \_\_\_\_\_

Average exposure temperature ( °C): \_\_\_\_\_

Drying time (minutes): \_\_\_\_\_

### C.1 Sample 1

	Machine direction (MD)	Transverse direction (TD)
Initial length (mm)		
Final length (mm)		
Percent shrinkage		

### C.2 Sample 2

	Machine direction (MD)	Transverse direction (TD)
Initial length (mm)		
Final length (mm)		
Percent shrinkage		

### C.3 Sample 3

	Machine direction (MD)	Transverse direction (TD)
Initial length (mm)		
Final length (mm)		
Percent shrinkage		

### C.4 Sample 4

	Machine direction (MD)	Transverse direction (TD)
Initial length (mm)		
Final length (mm)		
Percent shrinkage		

**C.5 Sample 5**

	Machine direction (MD)	Transverse direction (TD)
Initial length (mm)		
Final length (mm)		
Percent shrinkage		

**C.6 Averages**

	Machine direction (MD)	Transverse direction (TD)
Initial length (mm)		
Final length (mm)		
Percent shrinkage		

## Appendix D.—Wettability Measurement Data Form

Date: \_\_\_\_\_

Experimenter: \_\_\_\_\_

Material ID: \_\_\_\_\_

### D.1 Physical Description

Color _____ _____
Clarity _____ _____
Tack _____ _____
Flaws _____ _____ _____

Sample thickness (including carrier)

_____ _____ minimum: $t_{\min} =$ _____
---

Area, cm<sup>2</sup> \_\_\_\_\_

Temperature, °C \_\_\_\_\_

### D.2 Results

Time to wet sample: \_\_\_\_\_

Raw data stored in: \_\_\_\_\_

Instrument used: \_\_\_\_\_

### D.3 Notes after test

Sample appearance: _____ _____ _____ _____
---





## Appendix E.—Conductivity Measurement Data Form

Date: \_\_\_\_\_

Experimenter: \_\_\_\_\_

Material ID: \_\_\_\_\_

### E.1 Physical Description


Sample thickness (including carrier)


Minimum:  $t_{\min} =$  \_\_\_\_\_

Conductivity Cell ID \_\_\_\_\_

Cell gap correction:  $t_{\text{correction}} =$  \_\_\_\_\_

Shim thickness:  $t_{\text{shim}} =$  \_\_\_\_\_

Foil Carrier thickness:  $t_{\text{foil}} =$  \_\_\_\_\_

Net sample thickness:

$$t_{\text{NET}} = t_{\text{shim}} - t_{\text{foil}} - t_{\text{correction}}$$

$t_{\text{NET, cm}} =$  \_\_\_\_\_

Area,  $\text{cm}^2$  \_\_\_\_\_

Cell constant,  $\text{cm}^{-1}$   $k = t_{\text{NET, cm}} / A, \text{cm}^2$

$K, \text{cm}^{-1} =$  \_\_\_\_\_

## E.2 Results

Raw data stored in: \_\_\_\_\_

Instrument used: \_\_\_\_\_

Data:  $\sigma = k/R$

Date	File Name	T (°C)	R (ohms)	$\sigma$ (S/cm)

<b>Teardown Notes</b> _____ _____ _____ _____ _____ _____ _____
---

## References

1. M. A. Manzo, et. al., *Energy Storage: Batteries and Fuel Cells for Exploration*, 45<sup>th</sup> Aerospace Sciences Meeting and Exhibit, Reno, NV (2007).
2. W. Boehnstedt, in *Handbook of Battery Materials*, Besenhard, J. O., Ed., VCH Wiley, Amsterdam and New York, 1999.
3. P. Arora and Z. Zhang, *Chem. Rev.*, **104**, 4419 (2004).
4. R. Spotnitz, in *Handbook of Battery Materials*, Besenhard, J. O., Ed., VCH Wiley, Amsterdam and New York, 1999.
5. S. Zhang, *J. Power Sources*, **164**, 351 (2007).
6. R. S. Baldwin, NASA /TM-2009-215590 (2009).
7. R. S. Baldwin and W. R. Bennett, 4th International Energy Conversion Engineering Conference (IECEC), San Diego, CA (2006).
8. K. P. Menard, *Dynamic Mechanical Analysis a Practical Introduction*, CRC Press, 2008.
9. W. J. Schell, in *Battery Conference on Applications and Advances, 1999, The Fourteenth Annual*, pp.161-169, Long Beach, CA (1999).
10. E. P. Roth, et. al., *J. Power Sources*, **174**, 579 (2007).

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