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Properties and Performance Attributes of Novel Co-extruded Polyolefin Battery Separator Materials

Part 2: Electrical Properties

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September 2013

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Properties and Performance Attributes of Novel Co-extruded Polyolefin Battery Separator Materials
Part 2: Electrical Properties

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Abstract

As NASA prepares for its next era of manned spaceflight missions, advanced energy storage technologies are being developed and evaluated to address and enhance future mission needs and technical requirements. Cell-level components for advanced lithium-ion batteries possessing higher energy, more reliable performance and enhanced, inherent safety characteristics have been under development within the NASA infrastructure. A key component for safe and reliable cell performance is the cell separator, which separates the two energetic electrodes and functions to inhibit the occurrence of an internal short circuit but preserves an ionic current. Recently, a new generation of co-extruded separator films has been developed by ExxonMobil Chemical and introduced into their battery separator product portfolio. Several grades of this new separator material were evaluated with respect to dynamic mechanical properties and safety-related performance attributes, and the results of these evaluations were previously reported in “Part 1: Mechanical Properties” of this publication. This current paper presents safety-related performance results for these novel materials obtained by employing a complementary experimental methodology, which involved the analysis of separator impedance characteristics as a function of temperature. The experimental results from this study are discussed with respect to potential cell safety enhancement for future aerospace as well as for terrestrial energy storage needs, and they are compared with pertinent mechanical properties of these materials, as well as with current state-of-the-practice separator materials.

Background

As NASA embarks on a renewed human presence in space, human-rated electrical energy storage and power generation technologies that demonstrate reliable performance in a variety of unique mission environments will be required. To address the future performance and safety requirements, advanced rechargeable lithium-ion battery technology development has been pursued with an emphasis on addressing performance technology gaps between state-of-the-art capabilities and critical future mission requirements. Both cell and cell component development efforts have recently emphasized improving the safety characteristics, as well as the electrochemical attributes, of such battery systems in order to optimize their overall performance for manned space applications. Improved cell-level safety attributes are also important for advanced lithium-ion battery technologies that are currently under development for terrestrial and electric vehicle applications. A key cell component of a lithium-ion battery which significantly impacts both safety and electrochemical performance features is the battery separator.

The function and reliability of the separator are critical for the optimal performance and safety of a lithium-ion cell. 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, which would result in a short-circuit, and to allow the flow of ionic species within the cell. For battery safety, a 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. 1 and 2) have appeared in the literature, as well as some with a primary emphasis on lithium-based cell technologies (Refs. 3 to 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).

Presently, most commercially-available lithium-ion cell configurations that contain a liquid organic electrolyte employ a microporous polymeric membrane separator component, which provides cost-effective cell performance. These separators are based on polyolefin materials, such as polyethylene (PE), polypropylene (PP) and blends of such. Such polyolefin-based separators, which afford both excellent chemical stability and mechanical properties, are manufactured by either a wet or a dry process, both of which employ orientation steps to introduce porosity and increase tensile strength. Polyolefin battery separators made by the wet process are available from several sources, such as a widely used polyethylene-based material from ExxonMobil Chemical and its Japanese affiliate, Tonen Chemical. Commercial PE and PP films prepared by this process are available from Celgard, LLC (Ref. 2). Available grades of Celgard separators can be single layer PE or PP materials or a composite PP/PE/PP trilayer material.

Thermal Properties and Separator Shutdown Performance

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 (Ref. 7). 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 “thermal runaway” condition could occur, which would be a serious safety concern for a manned application.

For battery safety with lithium-based cell chemistries, especially for manned applications, it is desirable for a state-of-the-art battery separator to possess an inherent ability to shut the battery down (i.e., terminate the flow of electric current) if overheating occurs. The *shutdown* property of a polymeric separator material can internally provide a margin of safety against an external short-circuit, accidental overcharge or an abuse condition resulting in an elevated cell temperature. A separator’s shutdown mechanism can be summarized as follows: near the melting temperature of the specific polymeric material (e.g., 130 °C for PE), the micropores collapse, and this event is accompanied by a significant increase in both the separator and overall cell impedances, resulting in a moderation of electrochemical activity (e.g., the flow of ions) and current flow. Optimization of the shutdown response and efficiency may be achievable by tailoring material properties and processing methods. In a scenario where the internal temperature is rising rapidly, however, the separator film can melt, thereby eliminating the physical barrier separating the two electrodes.

The separator material should also possess high-temperature *melt integrity*, that is, to exhibit mechanical strength and robustness and resistance to polymer flow above the shutdown temperature, as characterized by a high *rupture temperature*. A rupture temperature characterizes the point when a separator sample has lost all of its mechanical integrity to form an insulating barrier between the two electrodes. After a separator shutdown occurrence, the cell temperature is likely to continue to increase. The separator must maintain mechanical integrity and high impedance at elevated temperatures in order to prevent the electrodes from making physical contact and creating the safety hazard of an internal short-circuit. Ideally, the mechanical integrity of the separator should be maintained for a long enough period of time for heat to be sufficiently dissipated and a thermal cool-down to occur. Dynamic Mechanical Analysis (DMA) can provide a measure of a material’s melt integrity. Representative results from DMA are illustrated in Figure 1, in which curves for both a monolayer Tonen polyethylene material and a multi-layer (i.e., PP/PE/PP) Celgard separator material are shown for comparison. For enhanced internal cell safety, separators with a rupture temperature greater than 150 °C are desirable for lithium-ion cells.

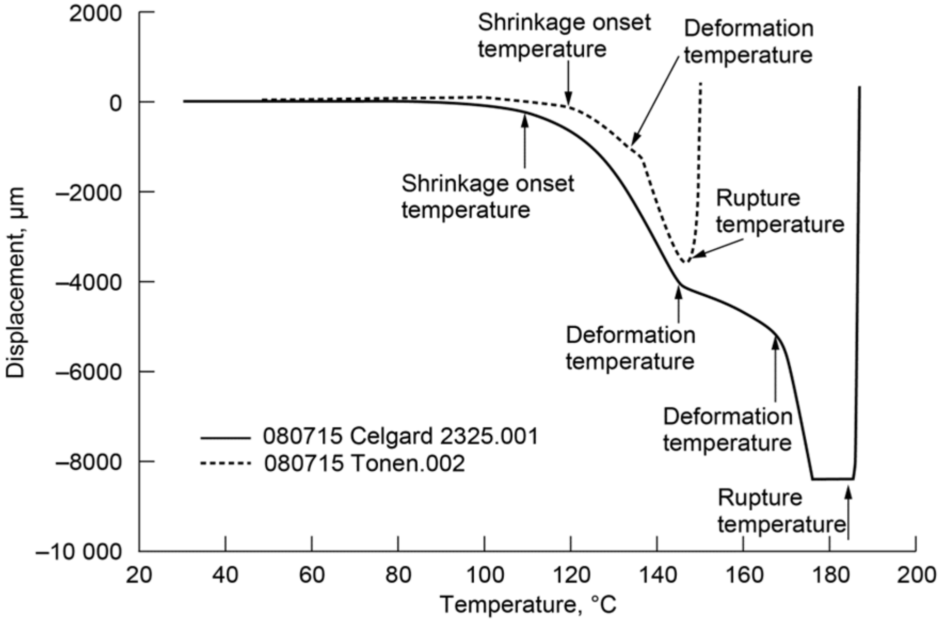


Figure 1.—Illustration of various temperature regimes for DMA melt integrity analysis (Ref. 8).

Co-extruded ExxonMobil Battery Separator Grades

In the 2006-07 timeframe, the introduction of novel co-extruded battery separator grades by ExxonMobil Chemical impacted the lithium-ion battery technology field by providing an innovative approach to enhancing cell-level performance. Based upon wet, bi-orientation process technology, the co-extruded polyolefin grades afford a new flexibility and versatility to the company’s commercial battery separator product portfolio, which had a heritage of mono-layer grades based upon polymer membrane technology attributed to their affiliate, Tonen Chemical. Tonen, which is based in Japan, had supplied the microporous film for the first lithium-ion battery introduced in 1991 by Sony.

The ExxonMobil co-extruded multi-layer separator materials, which are based on tailored, heat-resistant polymer formulations, feature significant improvements in both porosity, which leads to lower internal cell resistance, and thermal properties compared to their predecessors (Ref. 9). Improved thermal meltdown properties can extend the mechanical integrity of the separator film for a longer time during a thermal event, giving the cell more time to dissipate the generated heat, thus, decreasing the probability of a more catastrophic event. A summary of the co-extrusion process for polymeric film formation can be found in Reference 8.

Per company literature, the ExxonMobil Chemical/Tonen-developed film can retain the original shutdown temperature of the polyolefin material and retain the film’s mechanical integrity for an additional 40° Centigrade. By not melting until a higher temperature is reached, the new separator film provides more time for a malfunctioning cell to dissipate its heat before an internal short-circuit can occur, reducing the potential for transferring the heat to its neighbors and setting off a larger thermal event (Ref. 10). Enhanced thermal mechanical properties of the co-extruded grades are illustrated in Figure 2, which shows representative strain versus temperature data from ExxonMobil’s product literature. As illustrated in the figure, a larger temperature differential (i.e., safety enhancement) between the shutdown and meltdown temperatures is evident for the co-extruded material, although the two materials have similar visual appearances as the temperature is increased.

As reported in Reference 8, measures of the melt integrity of several of the novel ExxonMobil co-extruded separator grades were obtained by the DMA methodology described in the previous section, and the results for these materials are summarized in Figure 3.

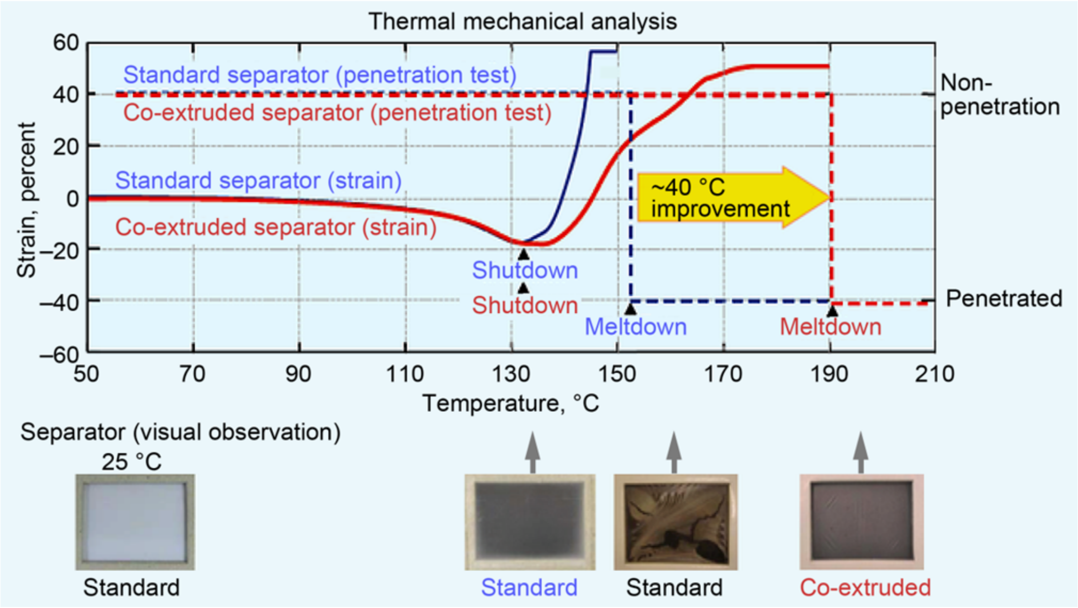
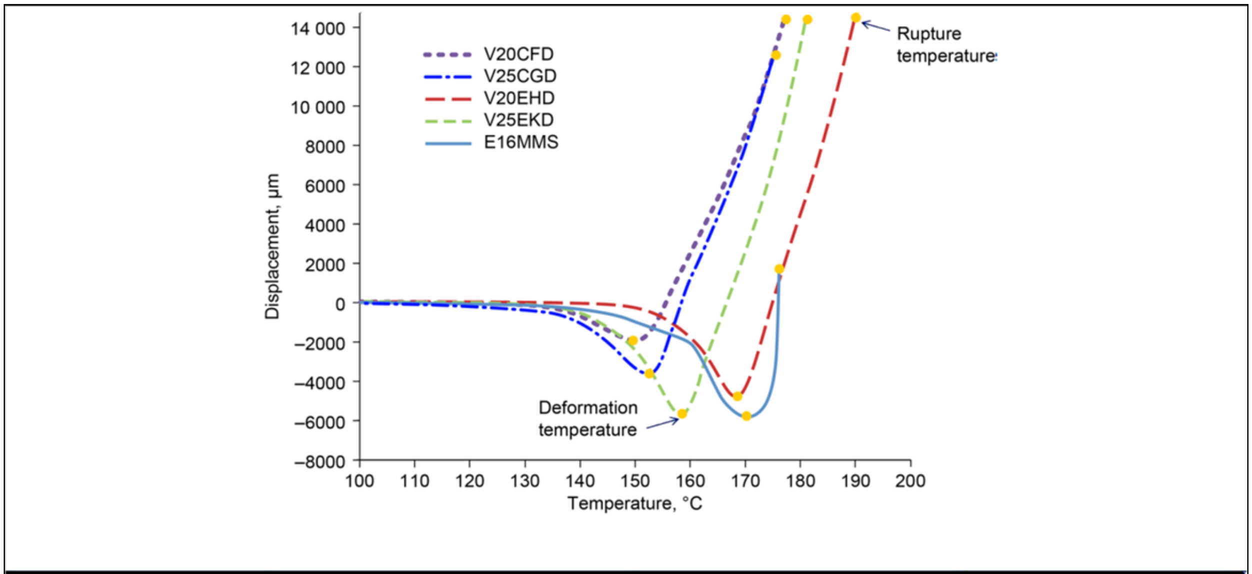


Figure 2.—Thermal mechanical properties of ExxonMobil/Tonen battery separator products (Ref. 10).



Material	Shrinkage Onset Temperature (°C)	Deformation Temperature (°C)	Rupture Temperature (°C)
V20CFD	125.38	150.15	178.38
V25CGD	129.34	153.8	181.4
V20EHD	157.3	167.7	191.1
V25EKD	142.68	162.92	183.63
E16MMS	121.35	160.3	173.06

Figure 3.—Example of experimental melt integrity data for ExxonMobil separator films from DMA analysis and corresponding tabulated average values of key temperature parameters (Ref. 8).

As summarized in Figure 3, a general trend for the co-extruded grades shows that for a grade with a higher observed deformation temperature, a higher rupture temperature was also observed. The V25EKD and the V20EHD materials exhibited the highest rupture temperatures of the four co-extruded grades. Also, after reaching the melting temperature, the different polymer formulations exhibit different strain responses, which are related to mechanical integrity, as the temperature increases to the point of film rupture. Recently, a similar DMA-based experimental methodology for assessing the durability of other commercial lithium-ion battery separator materials was reported in the literature (Ref. 11).

Experimental

Samples of the co-extruded polyolefin battery separator films under investigation in this report were obtained from the ExxonMobil Chemical Company, Macedon, New York. Experimental laboratory assessment results for key electrical properties for selected grades of co-extruded films, which are identified by ExxonMobil as V25EKD and V20EHD, are presented in this report. The numerical designation in the identification label signifies the nominal film thickness in microns (µm). For comparisons of the material properties and performance attributes of the new co-extruded grades to a state-of-the-practice separator, a microporous polyethylene Tonen SETELA (Tonen) separator, grade E16MMS was employed. This mono-layer grade, which has been produced in Japan since the early 1990’s, serves as a standard separator component in some lithium-ion cell designs. A comparison with a state-of-the-practice Celgard 2325 trilayer separator was also made.

All separator samples were inspected for uniform appearance and thickness, and were stored in a low relative humidity (<2 percent) dryroom environment. Mechanical and rheological properties relevant to separator integrity and performance in lithium-ion cells, such as puncture strength, thermal shrinkage, tensile strength and mechanical integrity at elevated temperature, were evaluated previously by Dynamic Mechanical Analysis (DMA) techniques using a TA Instruments Q800 Dynamic Mechanical Analyzer, and the results of these studies were reported in Reference 8. The electrolyte used in this study to impart ionic conductivity to the separator samples consisted of a 1M $LiPF_6$ salt in a 1:1:1 ratio of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) solvents, which is a standard lithium-ion battery electrolyte composition. Separator surface morphology studies were performed with a Hitachi Scanning Electron Microscope with X-ray analysis capability (SEM/EDAX).

Impedance Measurement Cell Fabrication

A modified 2325 coin cell configuration was employed as the cell fixture for conductivity and impedance (i.e., electrical resistance) measurements of electrolyte-wetted separator samples over the desired temperature range. This test configuration was selected as it provides a constant and reproducible pressure applied to a separator sample in a sealed-cell environment. The coin cell can and internal parts were initially inspected for any defects, sharp edges were removed from the stainless steel spacer electrodes and the metallic cell components were cleaned with solvent in a dry-room environment. The cell components were transferred to an argon-atmosphere glovebox for cell assembly. The sample separator material, which was previously dried for 12 hr under vacuum at 60 °C and stored in the glovebox, was punched to form the sample disc geometry, and its thickness was measured with a Mitutoyo Series 543 digital indicator, or equivalent.

After the addition of sufficient liquid electrolyte (~40 µl) to completely wet the separator sample and after the correct stacking sequence of the coin cell internal parts, as shown in Figure 4, a pneumatic coin cell crimper (National Research Council Canada 2325 Coin Cell Crimper System), as shown in Figure 5, was used to seal the coin cell while inside the inert-atmosphere glovebox.

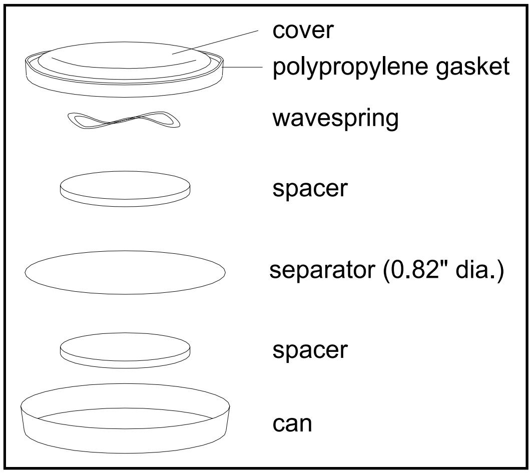


Figure 4.—Coin cell component stacking sequence.

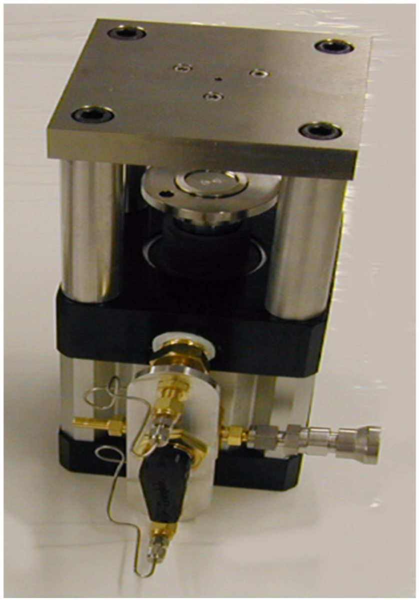


Figure 5.—Coin cell crimper system.

In most experiments, the integrity of a standard polypropylene grommet seal for sealing the coin cell can and cover together was sufficient at the elevated temperatures encountered during the separator measurements. A Zytel nylon gasket was also evaluated for this purpose, as it has higher temperature stability. After the assembled and sealed coin cell was removed from the glovebox and cleaned with ethanol, flat nickel metal strip tabs were carefully spot-welded with a Unitek Model Dual Pulse 125 welder to the cell’s two conductive surfaces to serve as electrical connections.

Separator Ionic Conductivity Measurements

Following coin cell fabrication, the internal electrical continuity of the sealed conductivity cells and the room-temperature ionic conductivity of the electrolyte-wetted separator sample were measured by an electrochemical impedance spectroscopy method described in detail earlier (Ref. 12). Measurements were made with a Solartron 1260 frequency response analyzer coupled to a Solartron 1287 electrochemical interface, and the operation of these instruments was automated using Scribner and Associates Zplot and Zview software for Windows (Microsoft Corporation). 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 were referred to for the separator impedance measurements utilizing the coin cell fixture. Generally, the impedance of the separator sample was measured over a frequency range of 0.1 to 10 kHz to characterize the material. Often, a single frequency measurement (e.g., at 1 kHz) is satisfactory for material screening purposes. At this frequency, the separator impedance was assumed to be equal to the separator resistance. After completion of desired conductivity measurements, the coin cell was weighed and prepared for studying the response of the separator sample resistivity to increasing temperature, as described earlier (Ref. 12).

High-Temperature Separator Integrity Measurements

The general methodology employed in this study of a separator's electrical response to a dynamic thermal environment for the evaluation and comparison of commercial and exploratory lithium-ion battery separator materials has been utilized for several decades (Refs. 13 and 14). In this study the coin cell test fixture was placed in a Tenny environmental chamber for controlling the sample's temperature environment during a test. The actual temperature of the coin cell, which had a fast-response Type-K thermocouple taped to its external surface, was monitored through an auxiliary channel of an Arbin Instruments BT-2000 battery test system, which is shown in Figure 6. During a test, the internal chamber temperature was ramped at the maximum rate that the Tenny can deliver, i.e., to try to mimic an actual thermal abuse event that might occur with a real battery. This rate was found to be ~4 °C/min in the 23 to 100 °C range, and ~2 °C/min at the higher temperatures employed in this study. During a test, a 50 SCFH flow of nitrogen gas is flushed through the chamber.

The Arbin instrument was used to monitor and acquire the data related to a coin cell's electrical response during a temperature ramp. Electrical connections to the coin cell tabs employed a 4-wire design for the application of a small (5 mA) current and for voltage response sensing. In Figure 7, three views of a wired coin cell within the Tenny environmental chamber are shown. A relative measure of the internal resistance of the coin cell test fixture, which was proportional to the impedance/resistivity of the enclosed separator sample, was performed by a two-step Arbin test schedule employing a "rest" period followed by an internal resistance measurement. The steps were repeated until the test was manually terminated. The Arbin software calculated the internal resistance by an IR pulse method employing multiple, fast current pulses and analyzing the corresponding voltage responses.

Figure 6.—Arbin battery test system.

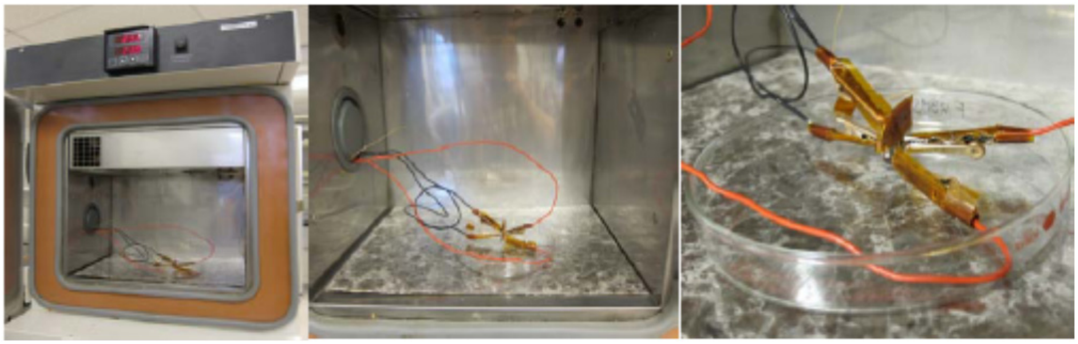


Figure 7.—A wired coin cell test fixture within the Tenny environmental chamber.

The specific test methodology utilized in this study included an initial equilibration of the coin cell test fixture at 23 °C in the environmental chamber and monitoring the cell's internal resistance for stability. The temperature was then ramped to a desired upper-limit, which was based upon the separator material's characteristics, while internal resistance data was continuously being collected by the Arbin test schedule.

Results and Discussion

The thermal response, shutdown properties and high-temperature integrity, as described in a previous section, for baseline and the ExxonMobil co-extruded battery separator grades of interest were characterized and studied by monitoring the relative resistivity/impedance of the electrolyte-wetted separator material while the temperature of the sample was being ramped. The specific grades of interest for this reported study were the ExxonMobil V25EKD and V20EHD grades, as well as a state-of-the-practice E16MMS grade. These specific materials were selected for comparison with the elevated-temperature mechanical integrity results obtained previously for these same materials by DMA techniques, as reported in Reference 8 and illustrated in Figure 3. The two other ExxonMobil grades previously studied by DMA were not included in this study, which had a focus on evaluating enhanced high-temperature melt integrity separator properties that are related to overall cell-level safety. The prior DMA studies showed that the ExxonMobil V20CFD and V25CGD grades were inferior to the two selected grades with respect to overall mechanical integrity at elevated temperatures (Ref. 8). The ExxonMobil literature indicates that these two grades were tailored for improving cell-level power performance by achieving a high permeability material property, whereas the V25EKD and V20EHD grades were tailored for enhanced thermal stability (Ref. 15).

The ionic conductivity measurements made on the fabricated coin cells containing the separator sample materials of interest were conducted for a qualitative assessment of electrical continuity within the sealed cells prior to subjecting them to the high-temperature integrity measurements, thus, the quantitative values observed are not reported here. In a few cases, an internal short-circuit was observed, and the cells in question were re-fabricated. The separator conductivity/resistivity values observed were in agreement with the literature values for the specific grades under investigation, which differed in thickness, porosity and related material properties.

High-Temperature Separator Integrity Results

For all of the separator samples examined in this study, a minimum of three separate cells were subjected to the test methodology. Typically, duplicate cells exhibited slightly different resistance responses to increasing temperature, with variations most likely attributed to changes in polymer material morphology as deformation continued. The agreement between the observed temperatures at which the onset of an internal short-circuit occurred was within approximately 5 percent for duplicate sample trials.

At this temperature extreme, the integrity of the coin cell test fixture is approaching its limit of reliability. Monitoring the resistance for several trials during a cooling down period from the maximum temperature indicated that the cell short-circuit event was permanent.

A representative graphical analysis of the data obtained from the high-temperature separator integrity experimental measurements is shown in Figure 8, with the Arbin data for the state-of-the-practice Tonen E16MMS separator being presented. Here, the measured internal coin cell resistance was plotted against the temperature as it was being ramped.

In Figure 8, a stable, low cell resistance is shown from room temperature up to ~130 °C, at which point the polyethylene separator began to melt (i.e., onset of the "shutdown" process). As the temperature increased and the material continued to melt, the pores for ionic conduction continued to close and the cell resistance dramatically increased. As the temperature increase continued above ~150 °C and the polymer deformed, flowed and shrunk dimensionally, the observed cell resistance began to decrease in response to morphology changes. The observed decrease in resistance may be indicative of the progressive opening of channels for ionic conduction in the material as it deformed. Between ~170 to 177 °C, which is identified with the "rupture temperature" for this test methodology, the cell resistance dropped to near zero, indicating that the separator sample had lost all of its mechanical integrity to form an insulating barrier between the two electrodes, and a "short-circuit" resulted. The response of mechanical strain with increasing temperature is illustrated in the DMA data curve for the E16MMS material shown in Figure 3. The result obtained from this impedance response methodology was also consistent with the "rupture temperature" observed via DMA analysis for the E16MMS separator material.

Experimental results of a duplicate trial for the Tonen E16MMS material are presented in Figure 9. In this trial, a Zytel coin cell gasket was used instead of a standard polypropylene gasket. The data shows less fluctuation in the observed resistance values with increasing temperature, possibly indicating that the seal integrity was better during the temperature ramp. However, examination of the cell fixture after completion of the trial showed a breech in the gasket seal, although the Zytel material itself had not melted. The plateau of relatively low resistance above 150 °C could be indicative of a return of ionic current flow within the cell after a non-sustaining shutdown had occurred.

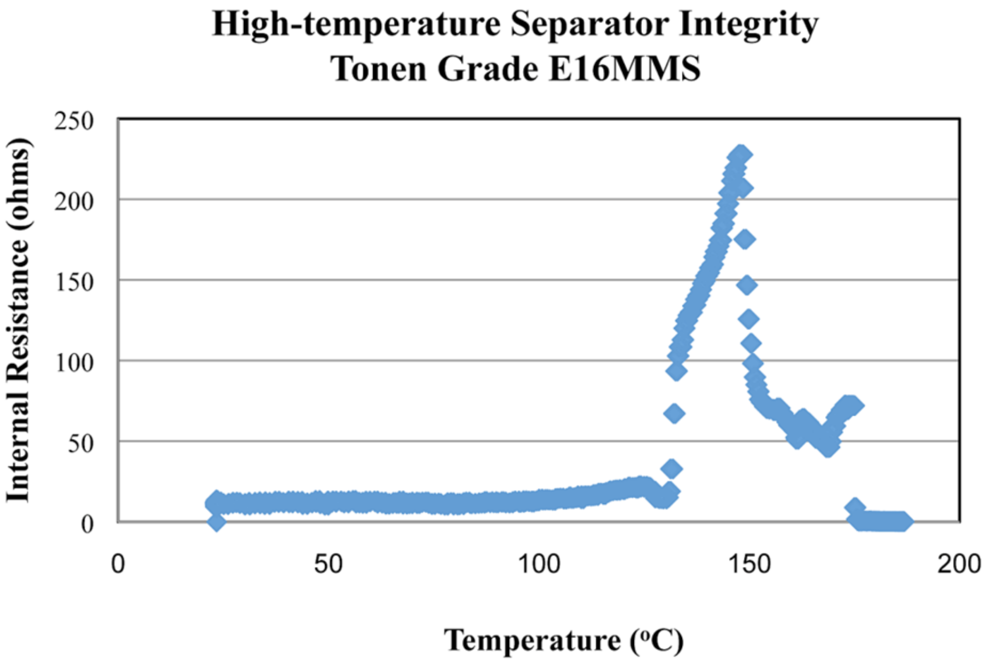


Figure 8.—Experimental high-temperature separator integrity data for Tonen E16MMS material.

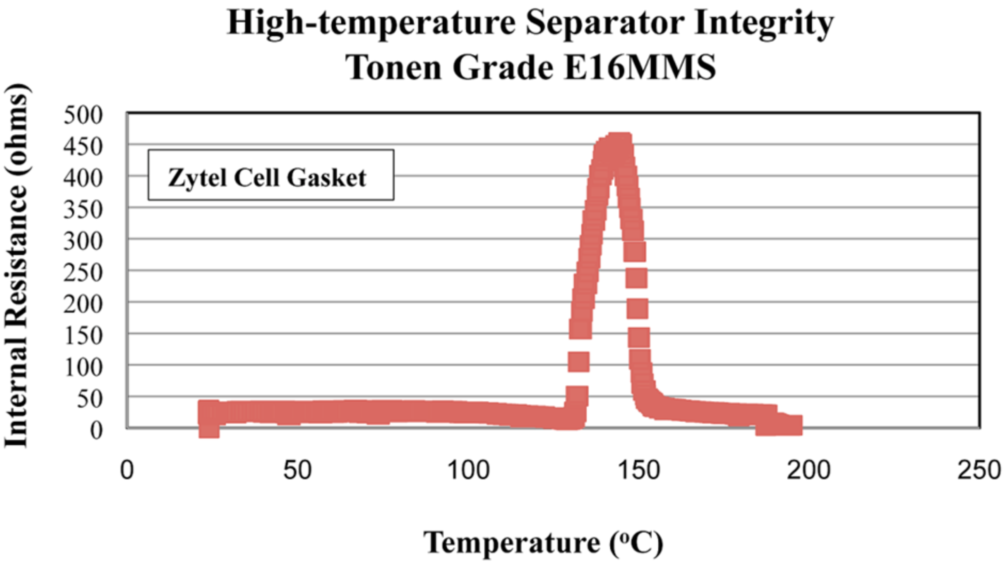


Figure 9.—Experimental high-temperature separator integrity data for Tonen E16MMS material with a Zytel cell gasket employed.

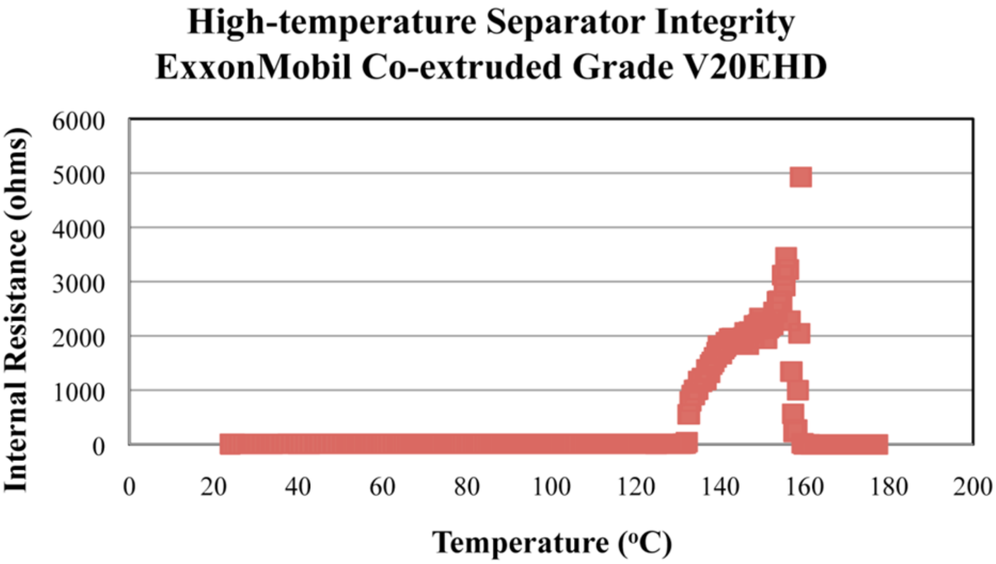


Figure 10.—Experimental high-temperature separator integrity data for ExxonMobil grade V20EHD material.

The experimental results for the two ExxonMobil co-extruded grades selected for this study are presented in Figures 10 and 11. The averaged results from viable duplicate sample trials for these material grades are shown in Figure 13, along with the experimental results from two state-of-the-practice separator materials.

The experimental results from this study for another state-of-the-practice polyolefin separator, Celgard 2325, are presented in Figure 12. The results for this trilayer material, which consists of a polyethylene layer sandwiched between two higher-melting polypropylene layers, shows the melting of the polyethylene layer at 132 °C followed by a shutdown event that is sustained with mechanical integrity for a length of time until the polypropylene layers begin to melt. However, the margin of safety (i.e., the difference in temperature between the onset of shutdown and the onset of the short-circuit event) appears to be less than for the co-extruded materials.

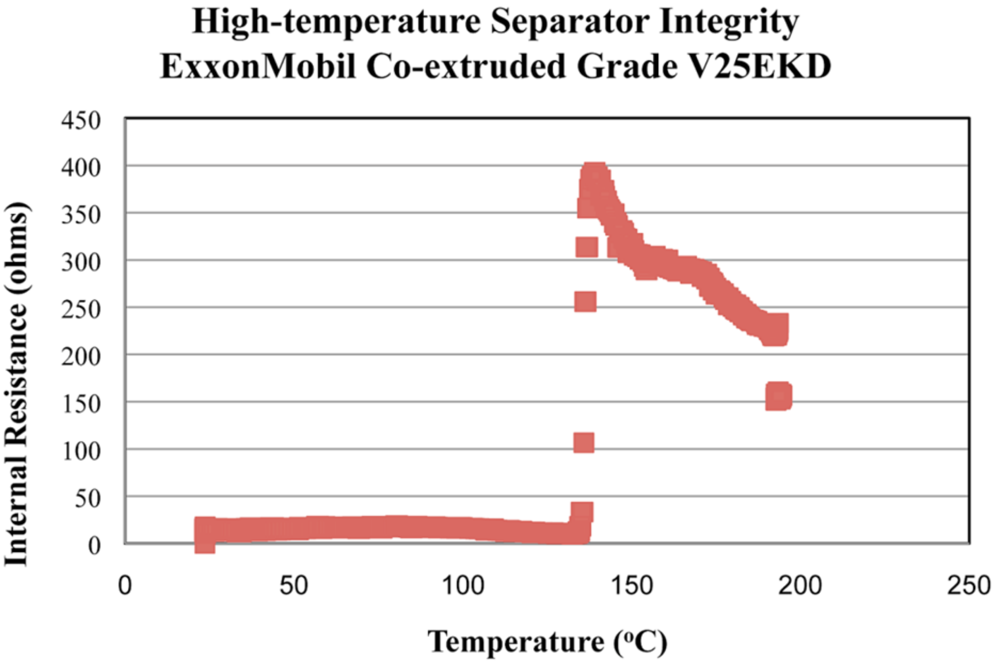


Figure 11.—Experimental high-temperature separator integrity data for ExxonMobil grade V20EKD material.

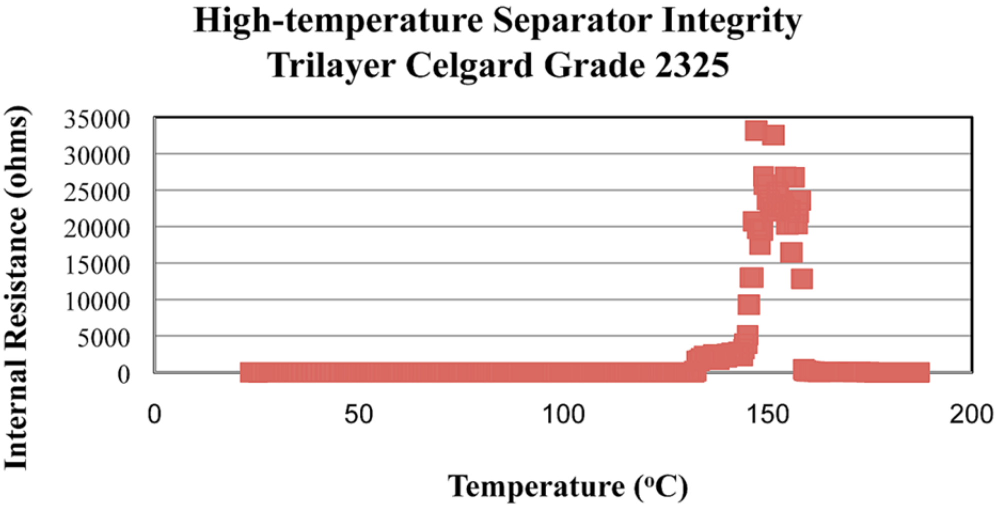


Figure 12.—Experimental high-temperature separator integrity data for Celgard 2325 separator material.

Comparison of Experimental High-temperature Separator Integrity Results for ExxonMobil Co-extruded and Baseline Lithium-ion Cell Separator Materials

Separator Grade	Separator Thickness (μm)	Initial Internal Resistance at 23°C (ohms)	Temperature at Onset of Shutdown Mechanism (°C) (Polymer Melting Temperature)		Temperature at Onset of Internal Cell Short-circuit (°C) (Rupture Temperature)	
			From Electrical (Impedance) Measurements	Literature Values for Melting Temperature	From Electrical (Impedance) Measurements	From Mechanical (DMA) Measurements
Tonen E16MMS	16	12	132	131	177	173
ExxonMobil V25EKD	25	15	135	134	175 to > 190	184
ExxonMobil V20EHD	20	10	133	134	172	191
Celgard 2325	25	10	132	134	176	181

Figure 13.—Tabulated experimental high-temperature separator integrity data for ExxonMobil and state-of-the-practice separator materials.

For both co-extruded materials, the two relevant experimental temperature values observed in this study are compared in Figure 13 with values representing the physical events as obtained from complementary investigations. The temperatures observed at the onset of the shutdown event were in excellent agreement with literature values, as well as with values observed from prior DMA studies. As illustrated in Figure 2 and discussed in Part 1 of this paper (Ref. 8), the shutdown event is correlated with the melting of the polymeric separator material and the experimental rheological observations associated with such. At the elevated temperature extreme representing the short-circuit event, reasonable agreement with DMA results was observed in this study for the V25EKD grade, however, a significant deviation was observed for the V20EHD grade. As only two duplicate trials of the V20EHD material were completed in this study, a specific reason for the discrepancy cannot be assessed from these preliminary results. Whether or not the test cell's internal electrolyte-soaked environment in this study contributed to the observed discrepancy for this material would necessitate further investigation. In general, the resistance responses observed after the polymer melting temperatures were reached indicate that the co-extruded materials were able to sustain relatively high resistance values (i.e., mechanical integrity) for a longer period of time before the onset of the short-circuit event, as compared to the monolayer Tonen E16MMS grade. The data shown in Figure 11 for one of the experiments with the V25EKD grade material is distinctive in that a total short-circuit was not observed up to the temperature limit for the Tenny environmental chamber, perhaps due to the remains of a physical barrier between the cell electrodes. Thermal mechanical analysis (TMA) results reported by ExxonMobil indicated that the V25EKD material maintained its melt integrity with little elongation against strain up to 190 °C (Ref. 9).

The enhanced thermal stability of the co-extruded separator materials was investigated by ExxonMobil during the heating process by atomic force microscopy and explained as follows (Ref. 9). When above the separator shutdown temperature, some of the polymer network appeared to remain unchanged while bulk material domains appeared to be imbedded within them. This suggested that the remaining networks acted as a skeleton and absorbed molten polymer domains in them, maintaining melt integrity at a high temperature.

Following the high-temperature cell internal electrical resistance measurements performed in this study, the coin cell containing the baseline E16MMS material and the cell containing the co-extruded V25EKD material, which was shown to possess a greater degree of high-temperature mechanical integrity compared to the baseline material, were disassembled for post-test analyses. The separator samples, which were both subjected to a temperature of >185 °C during their tests, were examined by SEM to elucidate surface morphology changes that occurred during the separator melting processes. In Figure 14, SEM photos of the E16MMS separator material are shown before heating (left photo) and after heating (right photo) during the test. The melted sample exhibited large pits, possibly due to vaporizing electrolyte, on the surface, and most of the polymer fibrils had fused together to form non-porous flat areas.

In Figure 15, SEM photos at x10 k magnification of the co-extruded V25EKD separator material are shown for an "as-received" (i.e., "pristine") sample and for the melted sample removed from the coin cell following the high-temperature test. Each pair of SEM photos shows both surfaces of the separator film.

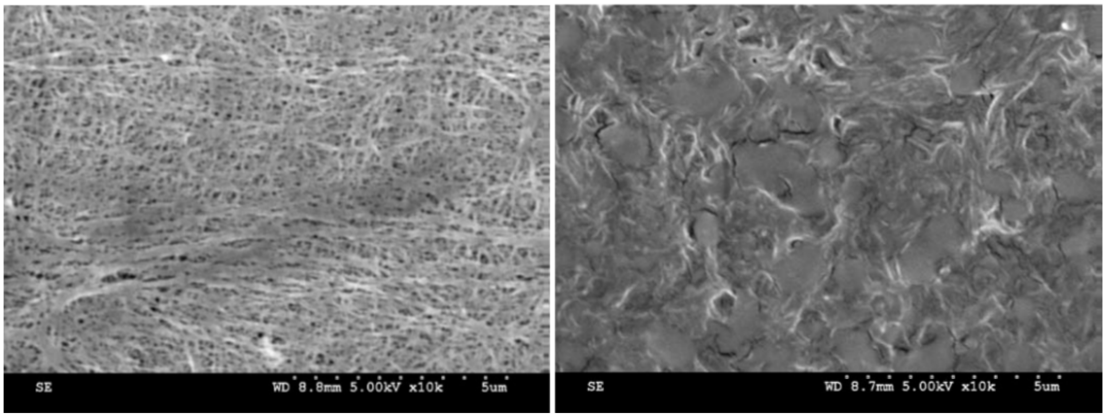


Figure 14.—SEM photos of Tonen E16MMS separator material before and after heating to >185 °C during the resistance measurement testing.

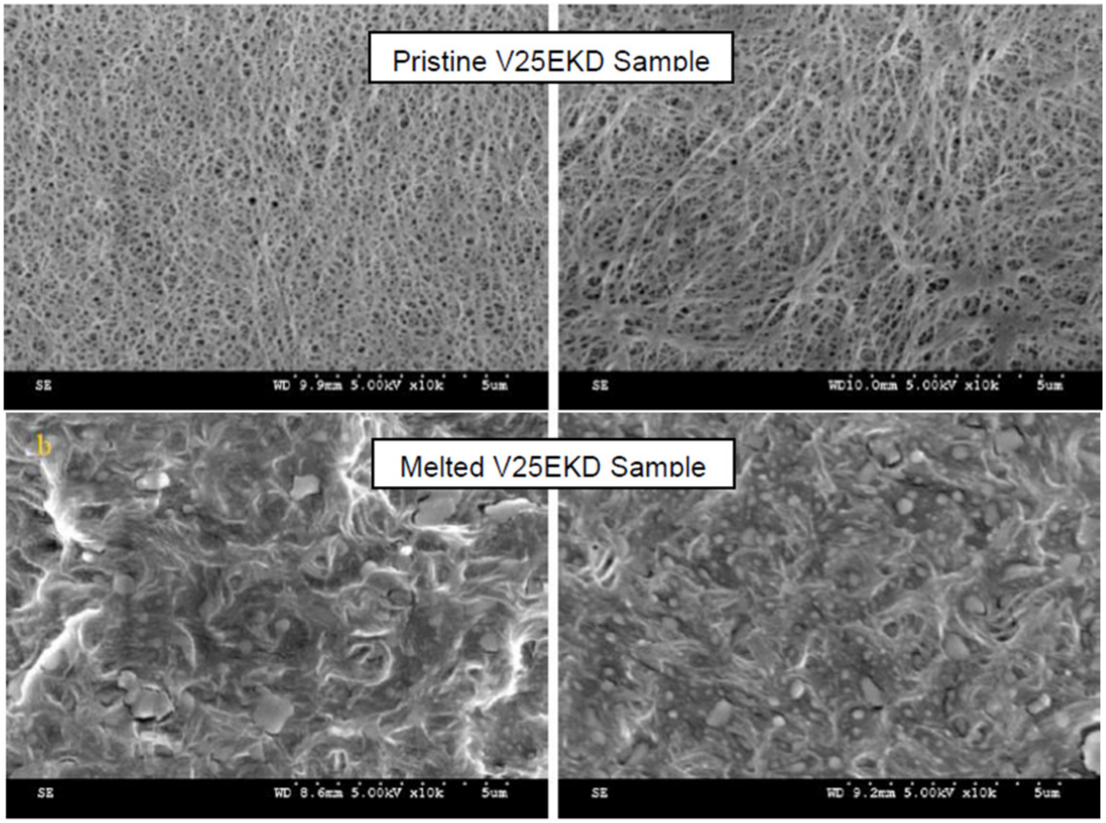


Figure 15.—SEM photos of ExxonMobil V25EKD separator material before and after heating to >185 °C during the resistance measurement testing.

In Figure 15, two different separator surface morphologies are evident in the SEM photos of the pristine V25EKD material, with differences in polymer fibril sizes and porosity exhibited. This observation is consistent with the co-extruded material being a multi-layered structure, with the individual polymer layers tailored to achieve the desired rheological properties of the composite material. In the SEM photos of both melted surfaces, small particles can be seen, which are most likely attributable to dried electrolyte salt crystals, imbedded within the fused polymer fibrils.

Conclusions

Comparing the two relevant observed temperature values in the table shown in Figure 13 for the different experimental methodologies, the laboratory assessment results for the electrical properties performed in this study for the ExxonMobil co-extruded polyolefin battery separators and the state-of-the-practice separator materials were in general agreement with prior results obtained by dynamic mechanical analyses methodologies, with the exception of the V20EHD grade, as discussed in the previous section. The methodology employed in this study, which was to analyze separator impedance characteristics as a function of temperature, utilized a test cell configuration that mimics to some degree a real battery/cell environment in which the separator component is flooded (i.e., wet) with electrolyte and an abusive event has caused the cell temperature to increase. The prior DMA study (Ref. 8) of the mechanical properties of these separator grades involved testing in a dry environment, and reasonable agreement between these two different experimental methodologies was shown for the V25EKD and the state-of-the-practice materials. Future experimental DMA techniques could be formulated to investigate more complex separator environments (e.g., an electrolyte-flooded condition) or pre-conditioning to afford a more detailed qualitative rheological interpretation of polymeric material responses to dynamic temperature changes. It is important to note that utilizing multiple complementary experimental methodologies for separator material characterization and performance assessments can afford a more complete understanding of mechanistic events and a more accurate quantification of the parameters related to these events.

The experimental methodology employed in this study was relatively easy to perform, and it can serve as a viable separator screening technique, although it could be refined with material and/or test cell design modifications to provide enhanced qualitative data on mechanical integrity in higher temperature regimes. The electrolyte composition chosen for this study is a standard lithium-ion battery electrolyte chemistry, but it lacks good thermal stability at temperatures above ~170 °C. The thermal decomposition of the $LiPF_6$ salt can result in the generation of gaseous products and pressure generation within a sealed cell, and the onset of exothermic reactions begin at ~200 °C (Ref. 16). In several experimental runs, the coin cell configuration did “vent” around the gasket, and it would be difficult to assess if the observed impedance response at the higher temperatures was influenced by such an event; however, an “infinite resistance” response was not observed, which would be indicative of a “dry” separator. It was also observed during the study that the integrity of coin cell test fixtures employing a Zytel nylon gasket was inferior to the integrity of cells with polypropylene gaskets at the higher temperatures.

Overall results from this study corroborate the more quantitative results and conclusion from the prior DMA investigations that the ExxonMobil co-extruded V25EKD grade material formulation may afford an enhanced level of internal safety-related performance and reliability for lithium-ion cell chemistries relative to some current state-of-the-practice cell separator component materials. In general, the improved meltdown properties of the co-extruded material, as shown by both impedance and DMA test methodologies, extend the integrity of the electrode-separating barrier for a longer time during a thermal event, allowing the cell additional time to dissipate heat and avoiding the occurrence of a more catastrophic event. Improved permeability attributes of these materials may also afford enhanced cell-level energy and power capabilities; however, a detailed cell-level model should be examined in order to assess potential performance advantages or disadvantages at the cell level relative to specific separator properties. For example, employing a thicker separator which may enhance cell-level safety will probably be at the expense of a lower achievable cell-level energy density.

In conclusion, the importance of enhanced safety attributes, which includes thermal safety, in new generations of lithium-ion battery separator materials, has been recognized in the battery technology development field for several years. This has been strongly driven by high-power battery development needs for electric vehicle applications. With a focus on future terrestrial needs, the U.S. Department of Energy (DOE) has solicited small business innovative research proposals with a specific objective of enhanced separator mechanical integrity at elevated temperatures, as well as funding other new efforts to address the development of thermally-stable separator materials and enhanced test methodologies for screening and evaluating their performance (Ref. 17).

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14. ABSTRACT

As NASA prepares for its next era of manned spaceflight missions, advanced energy storage technologies are being developed and evaluated to address and enhance future mission needs and technical requirements. Cell-level components for advanced lithium-ion batteries possessing higher energy, more reliable performance and enhanced, inherent safety characteristics have been under development within the NASA infrastructure. A key component for safe and reliable cell performance is the cell separator, which separates the two energetic electrodes and functions to inhibit the occurrence of an internal short circuit but preserves an ionic current. Recently, a new generation of co-extruded separator films have been developed by ExxonMobil Chemical and introduced into their battery separator product portfolio. Several grades of this new separator material were evaluated with respect to dynamic mechanical properties and safety-related performance attributes, and the results of these evaluations were previously reported in “Part 1: Mechanical Properties” of this publication. This current paper presents safety-related performance results for these novel materials obtained by employing a complementary experimental methodology, which involved the analysis of separator impedance characteristics as a function of temperature. The experimental results from this study are discussed with respect to potential cell safety enhancement for future aerospace as well as for terrestrial energy storage needs, and they are compared with pertinent mechanical properties of these materials, as well as with current state-of-the-practice separator materials.

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