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Short communication

Effects of separator breakdown on abuse response of 18650 Li-ion cells

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Abstract

The thermal abuse tolerance of Li-ion cells depends not only on the stability of the active materials in the anode and cathode but also on the stability of the separator which prevents direct interaction between these electrodes. Separator response has been measured as a function of temperature and high voltage both for isolated materials and in full 18650 cells. Separators with different compositions and properties were measured to determine the effect of separator melt integrity on cell response under abusive conditions. These studies were performed as part of the U.S. Department of Energy (DOE) Advanced Technology Development (ATD) Program.
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Keywords: Li-ion; Separator; Shutdown; Overcharge; Thermal runaway

1. Introduction

Separator thermal response and integrity plays a major role in determining the abuse tolerance of Li-ion cells. Shutdown-type separators are designed to impede ionic conductivity and thus shutdown electrical transport through the cell when the cell exceeds the melt temperature of one of the separator components. High cell temperature can result from several abusive conditions such as from external heat sources, short circuit or overcharge. The protection offered by the shutdown separator depends on the effectiveness of the shutdown mechanism, *i.e.* the magnitude of the impedance increase limiting the cell current, and the ability of the separator to maintain high impedance as a function of time while remaining at elevated temperature. An additional requirement for series connected cells is high-voltage stability after shutdown. A single high-impedance cell in a series string can be subjected to high potentials resulting from the remaining cells or from external power sources. Voltage breakdown of the separator can result in an internal short leading to thermal runaway and explosive cell failure.

We have measured the separator response of different separator materials both with and without shutdown properties. We have used overcharge as a strict abusive test to determine cell response during conditions of both over temperature and over voltage. Separator properties were also measured using a special fixture for determining separator impedance during a thermal ramp and also with high-applied potentials after shutdown. Full cell thermal abuse response is correlated with the separator properties determined by these methods.

These material and cell responses are being studied as part the U.S. Department of Energy FreedomCAR and Vehicle Technologies Office through the Advanced Technology Development (ATD) High Power Battery Development Program [1].

2. Separator measurements and techniques

Separators were chosen from commercially available materials that have been widely used in the battery community or are soon becoming available. The separators reported here include Celgard Trilayer shutdown separator and SEPARION® (Degussa) non-shutdown separator. The Celgard material is a shutdown separator consisting of three layers of polypropylene (PP) and polyethylene (PE) in a PP/PE/PP configuration while the Degussa SEPARION® material is a single layer of polyethylene terephthalate (PET) impregnated with alumina/silica.

Separator impedance as a function of temperature was measured using a multi-frequency impedance analyzer while the separator material (soaked in electrolyte) was maintained under constant pressure between parallel Ni electrodes. This device was also used to apply high potentials at elevated temperatures to determine the high-voltage breakdown limits of these mate-

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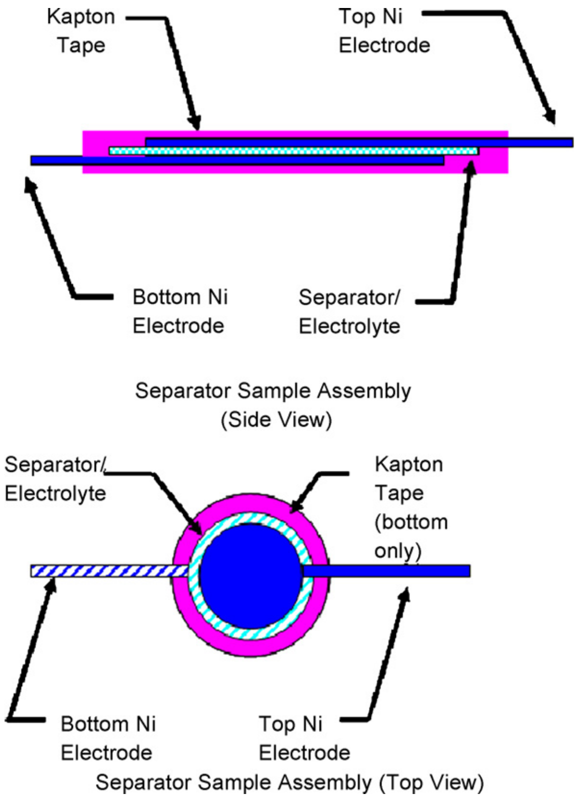

Fig. 1. Separator sample assembly for impedance measurements showing separator/electrolyte layered between Ni electrodes and sealed with Kapton tape.

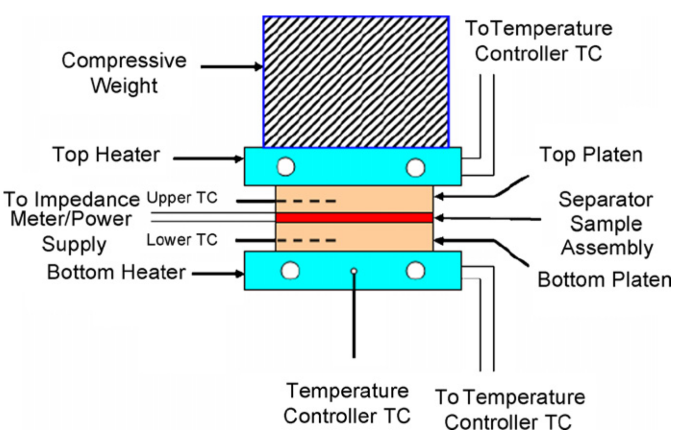

Fig. 2. Separator measurement fixture showing separator sample assembly between heated platens.

rials. Fig. 1 shows a schematic representation of the separator materials under test while Fig. 2 shows the measurement fixture. Separator impedance was measured as a function of frequency, excitation voltage, load pressure and temperature scan rate.

3. Separator characterization

The impedance profile for the Celgard trilayer material measured at 10 kHz is shown in Fig. 3. Shutdown was observed at 130 °C due to the PE melt followed by reduction in impedance at 155 °C due to the melt of the PP layer. High voltage integrity

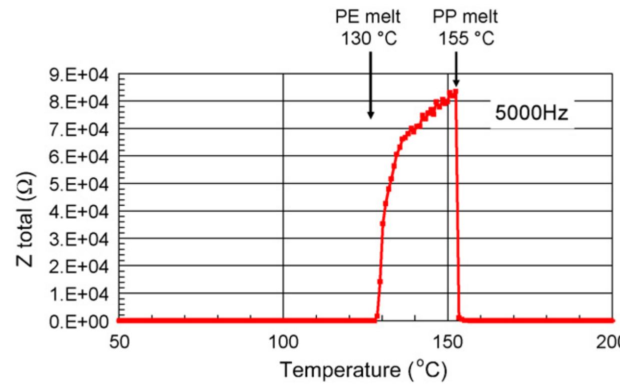

Fig. 3. Impedance (5 kHz) of Celgard Trilayer separator as a function of temperature (3° min^{-1} ramp rate).

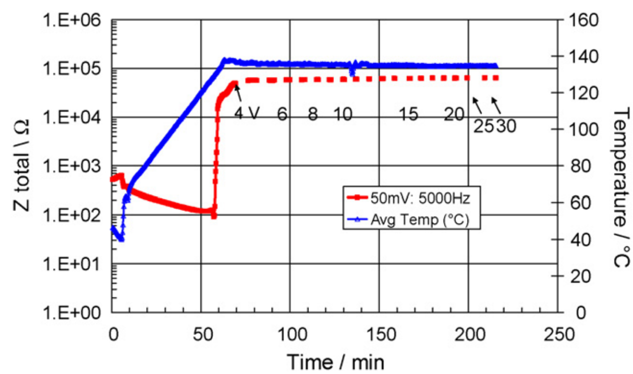

Fig. 4. No change in impedance after brief exposure to voltages up to 30 V.

was measured at temperatures above the shutdown temperature by applying increasing potentials up to 30 V for 1 min followed by an impedance measurement. As shown in Fig. 4, the separator does not show any degradation for these brief exposures to high voltage indicating that the separator material does not undergo an intrinsic high voltage breakdown at these potentials. Measurements of dc impedance up to 200 V for brief periods also did not show any signs of breakdown. However, continued exposure to elevated potential eventually results in degradation of the separator as indicated by the decrease in the dc impedance and eventual short circuit through the separator material layer as shown in Fig. 5. Increasing potentials and higher temperatures

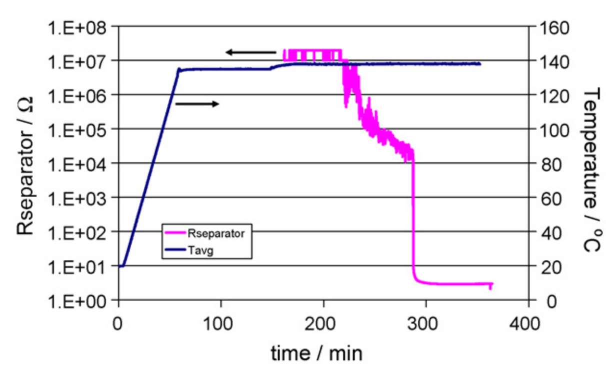

Fig. 5. Eventual breakdown preceeded by slow degradation of cell dc resistance (>2 h).

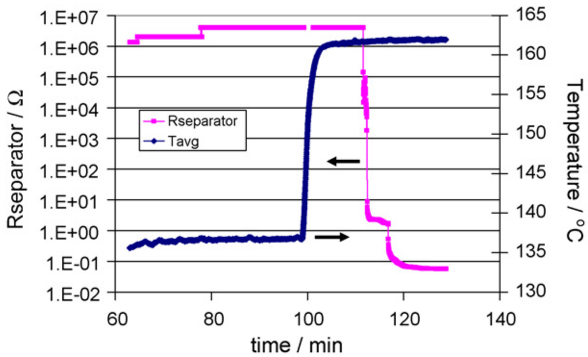

Fig. 6. Impedance of Celgard separator after ramp to temperatures above the PP melt temperature and the resulting short circuit failure of the separator after 8 min.

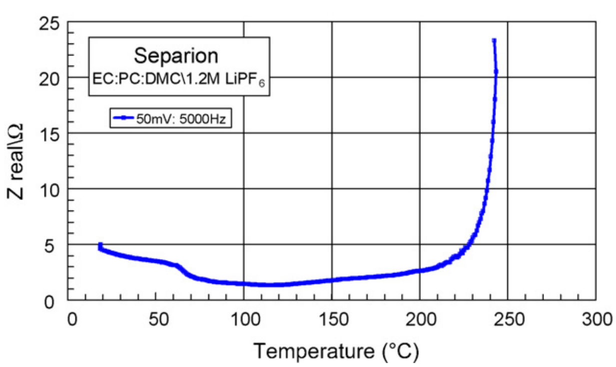

Fig. 7. Impedance profile of SEPARION® separator during a thermal ramp to 250 °C showing the non-shutdown, high-temperature stability of the separator.

reduce the time to failure of the separator material. Fig. 6 shows the dc impedance of the Celgard separator taken to the melt temperature of the PP component while under a 4 V potential. The impedance remained high and steady for 40 min at a temperature just above the PE melt temperature of 135 °C but shorted only 8 min after being ramped to 160 °C. The step change in impedance suggests that intermediate pinholes formed before a large enough hole developed to allow direct electrode contact.

The Degussa SEPARION® material does not have any shutdown behavior and thus was not measured for high voltage breakdown. The impedance measured as a function of temperature is shown in Fig. 7. The impedance remained low to above 220 °C at which temperature the PET backbone began to soften.

4. Cell measurements and techniques

Full Li-ion cells of the 18650 configuration were wound using these separators. The cells were prepared using coated electrodes consisting of carbon-coated natural graphite (GDR) anodes, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathodes and EC:PC:DMC(1:1:3)\1.2 M $LiPF_6$ electrolyte. The cell capacities for these tests were nominally 1.4 Ah. The cells were overcharged at increasing rates in a special fixture designed to quantitatively measure cell heat generation while also allowing measurement of the vent gas species. The cells were measured in an enclosure to allow control of the atmosphere to test for combustible vent gas mixtures. Fig. 8

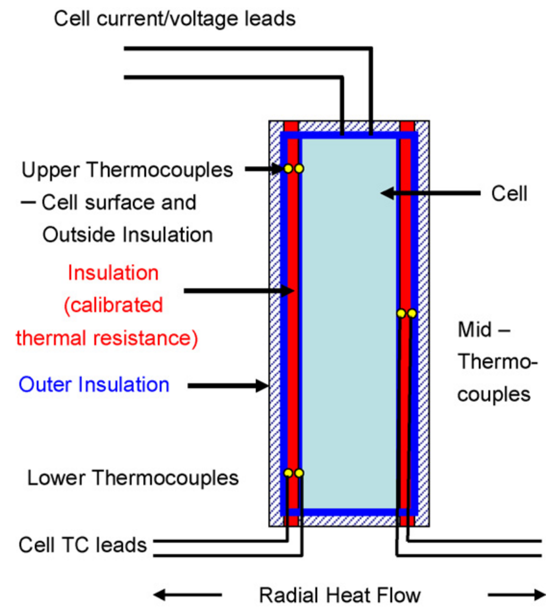

Fig. 8. Cell overcharge measurement fixture for determination of heat flow during overcharge and runaway.

shows a diagram of the overcharge measurement fixture while Fig. 9 shows a picture of the sealed enclosure.

The cells measured during overcharge experienced internal cell temperatures exceeding the melt temperature (135 °C) of PE used in some of these materials. When cells containing the PE-based separator exceeded this temperature, the full potential of the power supply appeared across the high impedance cell. The compliance voltage of the power supply was limited to 20 V and the cell response monitored over time. Thermal runaway was often associated with breakdown of the separator and the resulting internal shorting of the cell. Fig. 10 shows the cell temperature and charging current for a cell containing the Celgard shutdown separator that underwent shutdown but continued to conduct almost 200 mA with the applied 20 V potential. Although the cell temperature slowly decreased, the cell eventually started to develop an internal soft short and after 30 min developed a hard short leading to thermal runaway. Fig. 11 shows

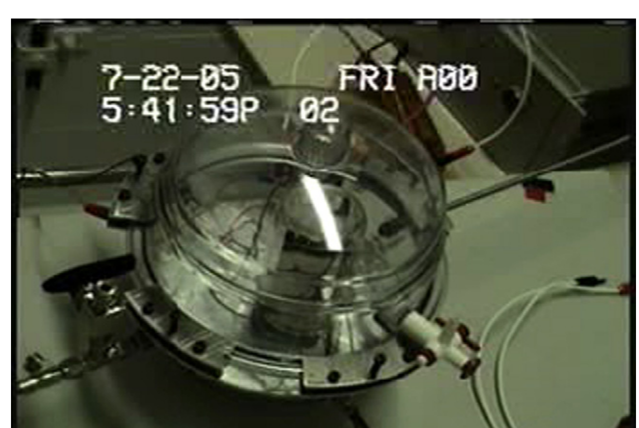

Fig. 9. Picture of cell overcharge fixture in the sealed enclosure.

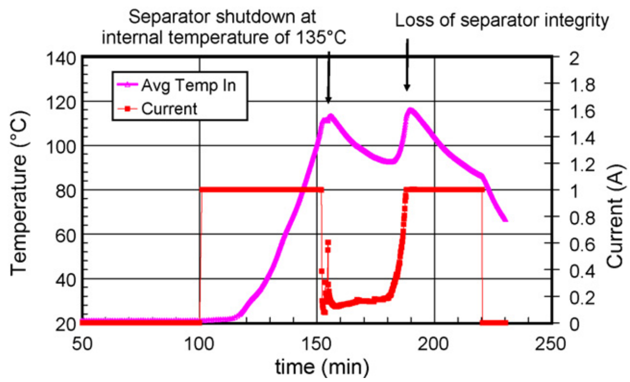

Fig. 10. Cell temperature and current profile during overcharge resulting in separator shutdown followed by delayed separator failure and runaway.

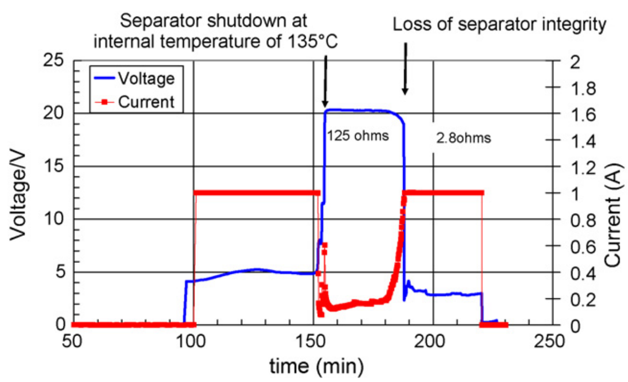

Fig. 11. Cell voltage and current profile during overcharge and subsequent runaway.

the developing current profile leading to the internal short and thermal runaway. Higher potentials across the cell after shutdown resulted in shorter times to separator failure and thermal runaway. Fig. 12 shows the voltage/current profile for an overcharge run using a 30 V compliance voltage. The cell remained in shutdown for only 3 min before failing. Cells in high-voltage modules can experience even higher voltages during some abuse events and undergo separator failure and cell thermal runaway almost immediately.

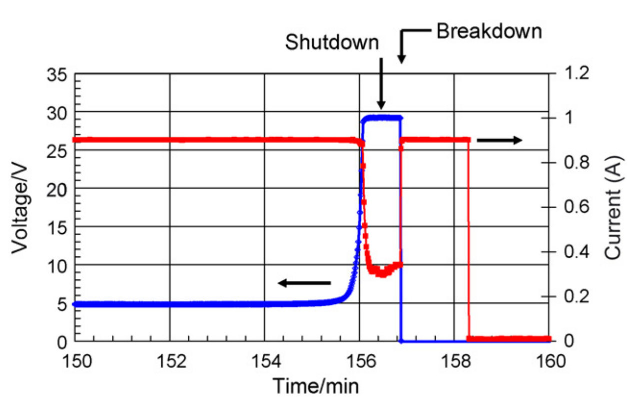

Fig. 12. Overcharge using higher power supply compliance voltage (30 V) resulting in more rapid separator failure and cell thermal runaway.

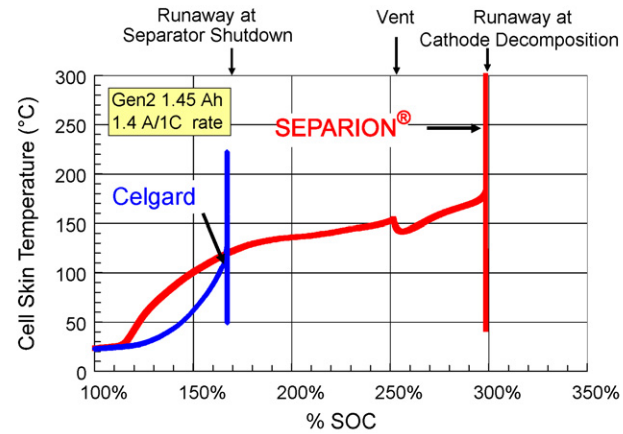

Fig. 13. Comparison of cell skin temperatures for cell with Celgard shutdown separator and cell with SEPARION® non-shutdown separator.

The overcharge performance of a cell without a shutdown separator was demonstrated using a cell manufactured using the SEPARION® non-shutdown separator from Degussa. The cell underwent a 1 C (1.4 A) overcharge as did the Celgard cells. The cell continued to heat during the overcharge but did not go into runway until the cell temperature reached 180 °C when the cathode underwent high-rate decomposition. This decomposition mechanism has been confirmed using accelerating rate calorimetry (ARC) of full cells and cathode only electrodes. At this charge rate, the SEPARION® separator cell was able to be overcharged to 300% state of charge (SOC) before runaway as compared to only 170% SOC for the Celgard separator. Different cell chemistries, charge rates and heat-transfer rates will result in different levels of overcharge before runaway but cells without a shutdown separator should always show increased range of overcharge (Fig. 13).

5. Conclusions

The separator in Li-ion cells has been shown to play a significant role in the overall thermal abuse tolerance of these cells. Shutdown separators can offer a degree of protection for single cells or small cell packs consisting of only a few cells connected in series. However, shutdown separators still do not completely block all conduction and the cells can undergo a delayed separator failure and internal short circuits resulting in thermal runaway. Series connected cells can result in high potentials across an individual cell that result in reduced time to failure. Overcharge has been shown to be a very abusive test of cell separator response. Cell heating during overcharge leads to separator shutdown and a delayed thermal runaway depending on heating rate and charging voltage. Non-shutdown separators were shown to allow overcharge until the cell temperature reached the runaway temperature of the cell components (cathode material for these cells). Improvements in separator shutdown properties are clearly needed and cells used in series-string cell modules may actually show increased overcharge tolerance without any shutdown separator in the cells.

Acknowledgments

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Reference

[1] The FreedomCAR program description can be found at: http://www.eere.energy.gov/vehiclesandfuels.