Thermal Shutdown Characteristics of Insulating Materials Used in Lithium Ion Batteries

B. N. Pinnangudi, S. B. Dalal, Noshirwan K. Medora, Ashish Arora, Jan Swart
Exponent Inc.,
23445 N 19th Avenue
Phoenix, AZ 85027 USA

Abstract- The lithium ion (Li-ion) battery market has undergone tremendous growth since its conception in 1990. Projections have indicated that the Li-ion battery market in the United States will top $9 billion in the next 3 years. Several factors including technical innovation, increased use of sophisticated consumer electronic gadgets and surge in high efficiency power sources for industrial applications have been the key in propelling the market demand for these products. Despite the positive trends, safety concerns related to the use of Li-ion batteries remain and may impact the market growth in future. Product recalls due to rechargeable batteries overheating and thereby posing a fire hazard to consumers have occurred as recently as April 2010. Research efforts have been undertaken to develop new separator materials with increased dimensional and thermal stability at high temperatures to make the Li-ion batteries safer for use. The separator is an electrically insulating polymer material that is engineered to have pores that allow lithium ions to shuttle back and forth between the battery's electrodes during the charge and discharge cycles. This paper presents an introduction to separator materials used in commercially available Li-ion batteries and a discussion of their thermal shutdown characteristics.

Index Terms: ***lithium ion, separators, thermal runaway, shutdown***

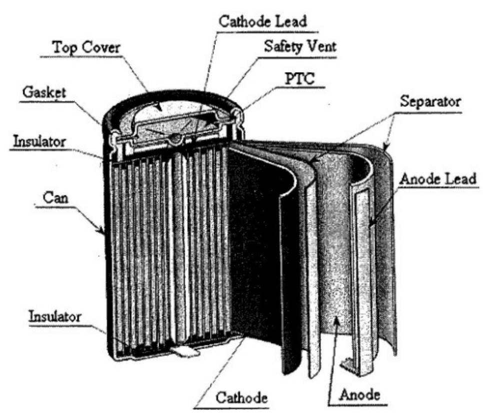
I. INTRODUCTION

The lithium ion (Li-ion) battery market has undergone tremendous growth since its conception in 1990. Projections have indicated that the Li-ion battery market in the United States will top $9 billion in the next 3 years [1]. Several factors including technical innovation, increased use of sophisticated consumer electronic gadgets and surge in high efficiency power sources for industrial applications have been the key in propelling the market demand for these products. Despite the positive trends, safety concerns related to the use of Li-ion batteries remain [2].

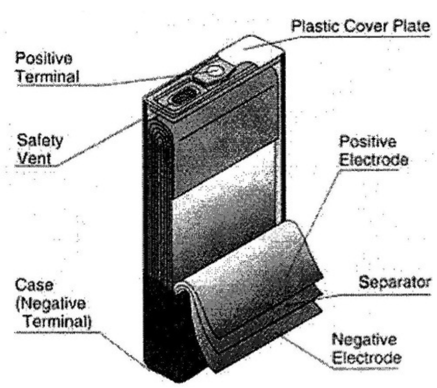
Product recalls due to rechargeable batteries overheating and thereby posing a fire hazard have occurred as recently as April 2010 [3]. Research efforts have been undertaken to develop new separator materials with increased dimensional and thermal stability at high temperatures to make the Li-ion batteries safer for use [4]. The separator is an electrically insulating polymer material that is engineered to have pores that allow lithium ions to shuttle back and forth between the battery's electrodes during the charge and discharge cycles.

II. BATTERY CONSTRUCTION

The construction of a cylindrically wound Li-ion cell and a wound prismatic cell are illustrated in Fig. 1. Wound designs are typical in small cells (<4 Ah). The cell construction consists of a positive electrode (10-25 µm aluminum foil coated with active material to a thickness of approximately 180 µm) and a negative electrode (10-20 µm cooper foil coated with a carbonaceous active material to a thickness of approximately 200 µm) separated by a 16-25 µm micro-porous separator in an electrolyte [5].



(a)



(b)

Fig. 1. (a) Cross sectional view of a cylindrical Li-ion cell and (b) a wound prismatic cell [5].

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A single tab (positive terminal – aluminum, negative terminal – Ni plated steel) at the end of the wind is used to connect the current collectors to their respective terminals. Commercially available Li-ion cells also incorporate safety devices that activate due to temperature or pressure such as positive temperature coefficients (PTCs), current interrupting devices (CIDs), and safety vents.

III. LI-ION CHEMISTRY

The active materials in the Li-ion cells operate in an intercalation process in which the Li ions are reversibly inserted and removed from the host without any significant changes to the structure of the host. The metal oxide and graphite with a layered or tunneled structure behaves as the host during the topotactic reaction. While charging, the positive material is oxidized (de-intercalation of Li ions) and the negative material is reduced (intercalation of Li Ions) as illustrated in Fig. 2 [6].

Positive: $$LiMO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_{1-x}MO_2 + xLi^+ + xe^-$$

Negative: $$C + xLi^+ + xe^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_xC$$

Overall: $$LiMO_2 + C \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_xC + Li_{1-x}MO_2$$

Fig. 2. Chemical reactions in a Li ion cell.

IV. SAFETY CONSIDERATIONS

Although rare, the Li-ion cells may go into thermal runaway and in some cases expel their contents. Fig. 3 shows a Li-ion battery pack after a failure occurrence. For this reason, the Li-ion battery packs are designed with multiple levels of protection at the cell level, pack level and in the host device. The safety protection can be accomplished by using either one or a combination of the following,

1. Integrated Circuits (IC) (primary and secondary),
2. Field effect transistors (FETs),
3. 3-terminal fuse,
4. PTC/CID,
5. Separator.

Fig. 3. Li-ion battery pack after a failure occurrence

V. POLYMER INSULATING MATERIALS (SEPARATORS)

The separator is a component in Li-ion batteries with liquid/gel electrolytes. The micro-porous polymeric separator membrane provides physical isolation between the electrodes while enabling free ionic transport and inhibiting electron flow. The separator itself does not participate in the cell reactions; however, its properties and structure may affect the overall battery performance, including but not limited to energy density, cycle life and safety. The separators in rechargeable Li-ion batteries are characterized by the following [7],

1. *Chemical stability*
   The separator material should be electrochemically stable under strongly oxidative and reductive environments, and simultaneously retain its mechanical strength.
2. *Thickness*
   High energy densities are associated with very thin separators. However, this adversely affects the mechanical strength and the safety. Hence, an appropriate selection of the separator thickness is necessary. Also, a uniform separator thickness increases the battery cycle life.
3. *Porosity*
   A high porosity is essential to maintain sufficient ionic conductivity between the electrodes. However, a porosity that is too high significantly affects the thermal shutdown performance as the pores cannot be effectively closed and the separator tends to shrink as it melts.
4. *Pore Size*
   The pore size should be selected such that it blocks the particles from the electrode components which include the active material and the conducting additives. Typically pore sizes in the micron range have been proven to be adequate.
5. *Permeability*
   Permeability is a measure of the electrical performance of the Li-ion battery. The lower the permeability the better is the battery performance in terms of safety and cycle life. Uniform separator permeability eliminates

uneven current distribution and is crucial for extending the cycle life of the battery.

6. *Wettability*
   The separator should be easily wettable in the electrolyte which facilitates electrolyte filling in the battery assembly and retain the electrolyte permanently to increase the battery cycle life.
7. *Thermal Shrinkage*
   The separator membrane tends to shrink with increasing temperatures due to the difference in the density of the crystalline and amorphous phases of the base material. An ideal separator should have no/minimum thermal shrinkage.
8. *Shutdown Performance*
   The separator should be capable of providing a shut down mechanism before reaching a threshold temperature at which the cell goes into thermal runaway. Also, the shutdown must occur without compromising the mechanical integrity of the separator which otherwise results in a direct contact between the electrodes and thereupon thermal runaway of the cell.

The separator material used in the current designs of a Li-ion battery are predominantly based on semi-crystalline polyolefin materials such as polyethylene (PE), polypropylene (PP), blend of PE and PP, high density PE and ultrahigh molecular PE. Synthetics including polyamide, polytetrafluoroethylene, PVDF, polyvinyl chloride and polyester have also been used as separator materials. Ceramic separators that combine the desirable characteristics of flexible polymers and ceramic materials are being increasingly preferred in upcoming cell designs [7].

VI. SEPARATOR CHARACTERIZATION

Prismatic cells rated for approximately 1 Ah supplied by five manufacturers (A – E) were chosen as the test samples for this study. All active/passive cell protection devices such as PTCs, thermal fuse etc. was bypassed during the test to prevent premature termination of the test before separator operation. These protection devices are generally external and can be bypassed relatively easily in prismatic cells, making them the cell of choice for the experiments. The following tests were performed to investigate separator operation and how they protected the cells from going into thermal runaway.

- High temperature storage test
- Heating test per UL1642 [8]
- Cell overcharge test

During the high temperature storage test, two cells each of manufacturer A and B were discharged to 2 V using a DC electronic load. The cells were discharged to 2 V to minimize the energy stored in the cell. The cells were soaked at 120˚C. The test was again repeated with different sets of cells at 125˚C, 130˚C and 140˚C. Two cells each of manufacturer A and B were used to account for data variability. The internal resistance of the cells was measured before and after thermal exposure using an impedance meter (1 kHz sine wave signal) and the results are shown in Fig. 4. It can be seen from Fig. 4 that the separator used in both the cell types (manufacturer A and B) are designed to operate in the 125˚C - 130˚C temperature range. The thermal shutdown of the separator is identified by the increase in the internal resistance by at least two orders of magnitude before and after thermal exposure.

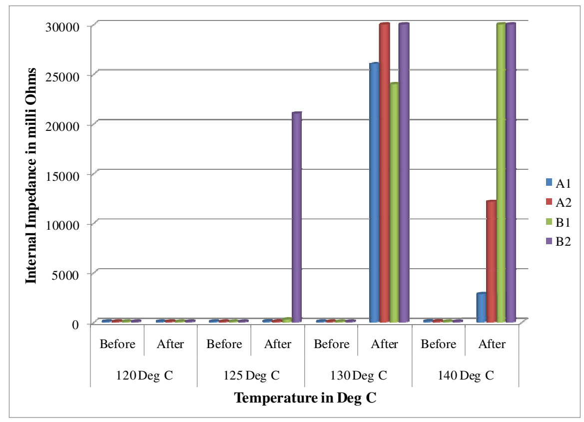

Fig. 4: Internal resistance of two cells each of manufacturer A and manufacturer B before and after thermal exposure

The heating test as per UL1642 and an overcharge test was performed to verify the results obtained above and to further evaluate the thermal shutdown performance of the separator. The UL1642 standard is a UL standard for evaluating the safety of Li-ion cells. The testing was performed on Li-ion cells of cell type 3-8 supplied by two manufacturers C and D. All the protection levels including the PTC/CID and thermal fuse were bypassed so that the separator was the only available protection mechanism to prevent cell thermal runaway.

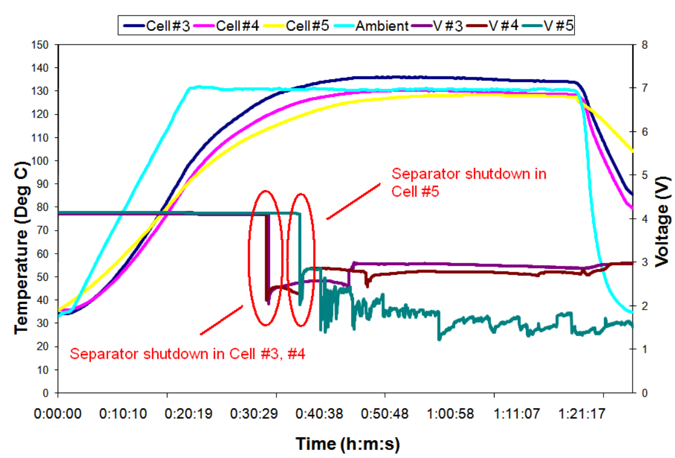

Fig. 5: Thermal shutdown performance of separators in three different cell types (3-5) supplied by manufacturer C.

The tested cells were heated in a gravity convection/circulating air oven at an initial temperature of 20 +/- 5˚C. The temperature of the oven was raised at a rate of 5

+/- 2˚C per minute to a temperature of 130 +/- 2˚C and was left to soak at this temperature for 10 minutes. The test samples were then cooled to room temperature and examined for thermal damage. The UL1642 standard requires that the cell does not catch fire or explode during the test. The test results are shown in Figs. 5-8.

It can be seen from Fig. 5 that the open circuit voltage of all the cells remains fairly constant until a threshold temperature beyond which the cell output voltage drops. The collapse in the output voltage is likely due to the separator shutting down. Similar results were obtained with cell type 6 supplied by manufacturer D as shown in Fig. 6. The threshold temperatures were consistent with the results obtained in Fig. 4.

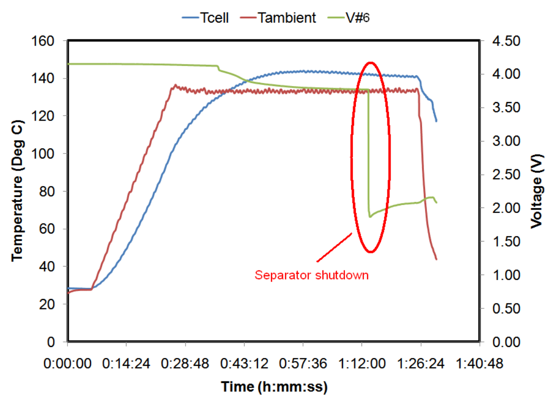

Fig. 6: Thermal shutdown performance of the separator in cell type 6 supplied by manufacturer D.

Fig. 7 and Fig. 8 indicate one cell type each of manufacturer C and D where the cell goes into thermal runaway. Unlike Fig. 5 and Fig. 6 where the cell temperatures stabilize once the ambient temperature ramp is stopped, it can be seen in Fig. 7 and Fig. 8 that the cell temperatures rise continuously to approximately 300˚C and 500 C respectively. This could be due to a variety of reasons. One reason can be that the separator within the cell may have failed resulting in an internal cell short circuit and resultant thermal runaway or alternatively, a chemical reaction may have started within the cell causing the cell to go into thermal runaway.

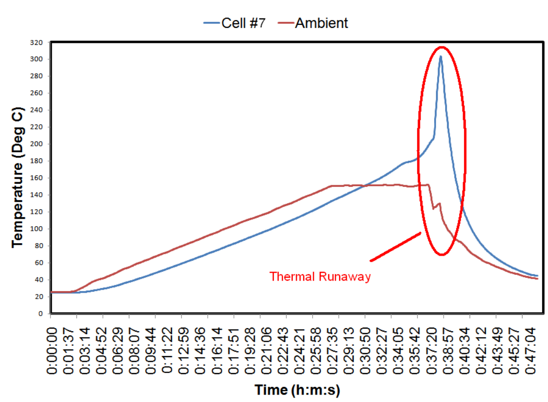

Fig. 7: Thermal runaway in cell type 7 supplied by manufacturer C.

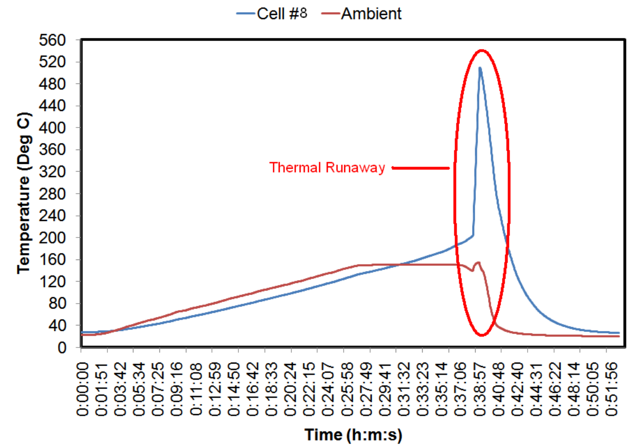

Fig. 8: Thermal runaway in cell type 8 supplied by manufacturer D.

The tests that were performed based on the UL1642 standard were strictly environmental; i.e. the cell was neither charged nor discharged during the test. The overcharge test was performed to determine whether the operation of the separator during overcharge conditions could prevent a cell failure. The assumption is that all the external protection circuits except the PTC/CID had failed. The protection could typically fail due to the application of an adapter with an incorrect output voltage. Cell types 9 and 10 supplied by manufacturer E were used as the test samples for the overcharge test.

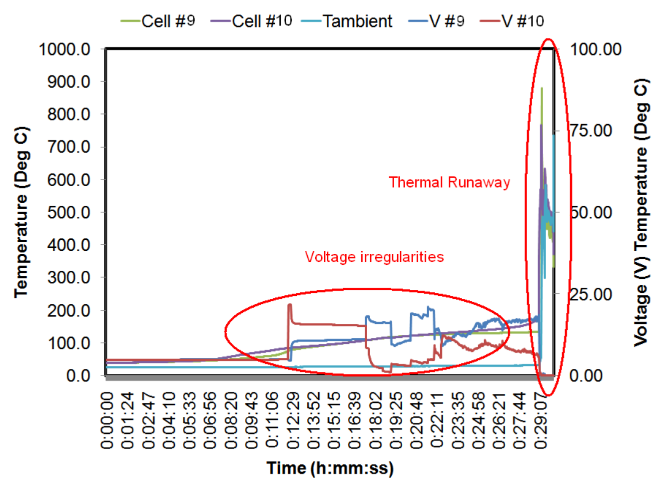

Fig. 9: Overcharge tests performed on cell types 9 and 10 supplied by manufacturer E.

The overcharge test was performed on a fully discharged cell. Since the aim of the test was to overcharge the cell and observe its response, an external power supply set to 30 Vdc and a current of 1 A (1 C charge rate) was used to charge the cell during the test. The test results are shown in Fig. 9. Fig. 9 shows that the overcharge condition caused the cells to go into thermal runaway. Again, the exact reason for this occurrence is not known and may range from an internal reaction before the separator shut down and stopped the charge current to a complete failure of the separator to terminate charge current. The peak cell temperature was recorded above 1000˚C during the test.

VII CONCLUSIONS

Li-ion cells, their construction, chemistry and safety concerns were briefly reviewed. The characteristics of separators and their application in a Li-ion cell were discussed. The thermal shutdown characteristics of a separator in different cell types supplied by five manufacturers were studied and their performance characterized.

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