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Characterization of thermal cut-off mechanisms in prismatic lithium-ion batteries

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Abstract

Lithium-ion (Li-ion) cells that are subjected to electrical abuse, overcharge and external short-circuit in particular, exhibit a rapid increase in cell temperature that could potentially lead to catastrophic disassembly of the cell. For this reason these cells are integrated or combined with one or more safety components that are designed to restrict or even prevent current flow through the cell under abusive conditions. In this work, the characteristics of these components in several prismatic Li-ion cells are studied by monitoring the impedance (*Z*) at 1 kHz and the open circuit voltage (OCV) of the discharged cells as a function of temperature. All the cells studied were found to use polyethylene-based shutdown (SD) separators that were irreversibly activated within a narrow temperature range between 130 and 135°C. In some cells irreversible cut-off was also provided by a current interrupt device (CID) or a thermal fuse. Both these devices had a circuit-breaker effect, causing the impedance of the cell to rise infinitely and the OCV to drop to zero. In addition to these irreversible cut-off mechanisms, some cells also contained internal or external positive-temperature-coefficient (PTC) devices that could provide current-limiting capability over a very wide temperature range. The interdependence of the thermal behavior of these components on each other and on other thermally dependant processes like cell venting, separator meltdown and weld joint failure are also discussed.

Keywords: Lithium-ion; Batteries; Safety devices; Thermal characteristics; Impedance

1. Introduction

As portable electronic products continue to proliferate into the marketplace, the demand for rechargeable batteries continues to skyrocket. Much of this demand is for lithium-ion (Li-ion) batteries, which can demonstrate energy densities that are 30–60% higher than competing chemistries like nickel–cadmium or nickel metal hydride systems [1]. In addition, Li-ion systems also provide longer cycle life and higher voltages when compared to the nickel-based systems. However, the presence of highly reactive electrodes and non-aqueous electrolytes in a fully charged Li-ion cell is cause for concern. For example, if a charged or over-charged Li-ion battery experiences temperatures in excess of 130°C it could vent with flame. At these elevated temperatures, reactions involving the active electrode material, electrode binder and the non-aqueous electrolyte lead to self-heating of the cell thereby causing the cell temperature to rise without further external heating [2]. This condition, usually referred to as the *thermal runaway* condition, could potentially lead to catastrophic disassembly of the cell.

An abnormal increase in cell temperature can occur from internal heating caused by either electrical abuse — overcharge or short-circuit — or mechanical abuse — nail penetration or crush. Higher cell temperatures could also be a result of external heating. Typical examples of external heating would be either a battery pack stored in the dashboard of a parked car in summer in a hot climate, or a battery pack that is thermally abused by heating or incineration. For this reason, battery packs containing Li-ion cells are designed with safety control circuits that have redundant safety features. In addition, the cell itself may contain safety devices that can be activated by high temperature, excess pressure, high current or some combination of the three. These components may either be integrated within the cell or attached externally without significant modification of cell dimensions and are primarily useful when the cell undergoes overcharge or external short circuit.

Thermal cut-off devices typically function by experiencing an increase in impedance in response to temperature increments. Small changes in impedance can limit the amount of current passing through the cell. Large changes

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in impedance may provide a circuit breaking effect, leading to a complete cut-off in the flow of current. Although the impedance–temperature relationships of these devices have been studied at a component-level [3,4], very few studies have focused on the activity of these devices in the cell when combined with each other. In the work described in this paper, the safety features provided by the thermally-activated components present in several discharged prismatic Li-ion cells were studied by monitoring the impedance (*Z*) and the open circuit voltage (OCV) of these cells as a function of temperature. Discharged cells were used so that thermal runaway reactions would not interfere with the experiment. The interdependence of the thermal behavior of these components on each other and on other thermally dependant processes like cell venting, separator meltdown and weld joint failure are also discussed.

2. Experimental

Fig. 1 shows a schematic of the experimental setup that was used to monitor impedance and OCV as a function of temperature. A VWR 1602 programmable oven was used to heat the cells at the rate of 2°C per minute from room temperature to 180°C. All cells were discharged to 3 V before they were placed in the oven for the thermal excursion. This was done to avoid any thermal runaway reactions during the experiment. Impedance was measured using a Hewlett-Packard 4338B Milliohmmeter and OCV was measured using a Hewlett-Packard 34401A Multimeter. Temperature measurements were made with a second HP Multimeter that was used in combination with a Fluke 80TK thermocouple module. Data from both multimeters and the milliohmmeter were acquired on a personal computer through HP Vee instrument driver software.

The cells used in this study were of the prismatic Li-ion type. Table 1 lists the weights and dimensions of all the cells. The cells are classified as A, B, C or D based on the supplier. The cathode material in the cells C1 and C2 was lithium manganese oxide ($LiMn_2O_4$). All other cells had a lithium cobalt oxide ($LiCoO_2$) cathode. Table 2 lists the rated capacity, OCV and impedance of all the cells.

Table 1
Weights and dimensions of Li-ion cell samples

Cell	Type	Weight (g)	Dimensions[a] (mm)
A1	Li-ion	23	6 × 30 × 47
A2	Li-ion	37	8 × 34 × 47
A3	Li-ion	37	8 × 34 × 46
B	Li-ion	39	9 × 34 × 47
C1	Li-ion	23	6 × 30 × 48
C2	Li-ion	37	9 × 34 × 48
Dl	Li-ion	22	6 × 30 × 48
D2	Li-ion	42	10 × 34 × 50

[a] Thickness × width × length.

Table 2
Capacity, impedance and OCV of Li-ion cell samples

Cell	Capacity[a] (mAh)	OCV[b] (V)	Impedance (mΩ)[c]
A1	550	3.44	148
A2	900	3.38	98
A3	950	3.51	49
B	900	3.37	54
C1	600	3.30	130
C2	1050	3.20	56
D1	600	3.64	65
D2	1400	3.41	87

[a] As rated by cell manufacturer.
[b] Open circuit voltage.
[c] Impedance measured at 1 kHz.

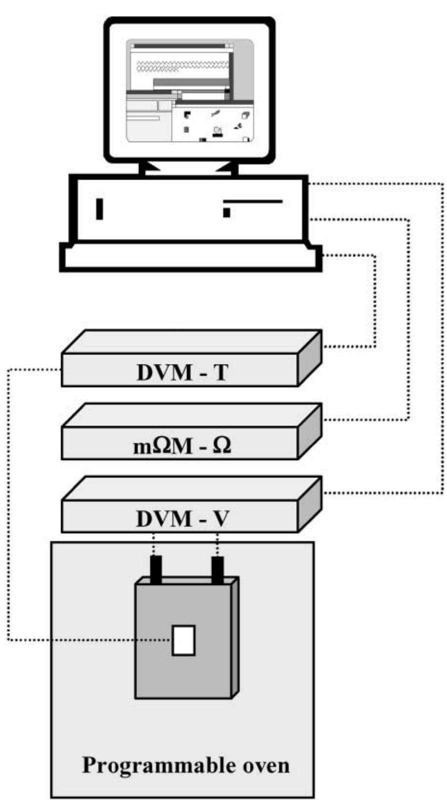

Fig. 1. Experimental setup for studying thermal cut-off mechanisms in Li-ion cells.

3. Results and discussion

In this section, we review the results of the impedance–temperature experiments and discuss the implications of the same. The purpose of these experiments is not to pass judgment on the relative safety of the cells but rather to highlight the usefulness of studying impedance–temperature and OCV–temperature behavior to get a better understanding for the thermal cut-off characteristics of the components or safety devices of the cell.

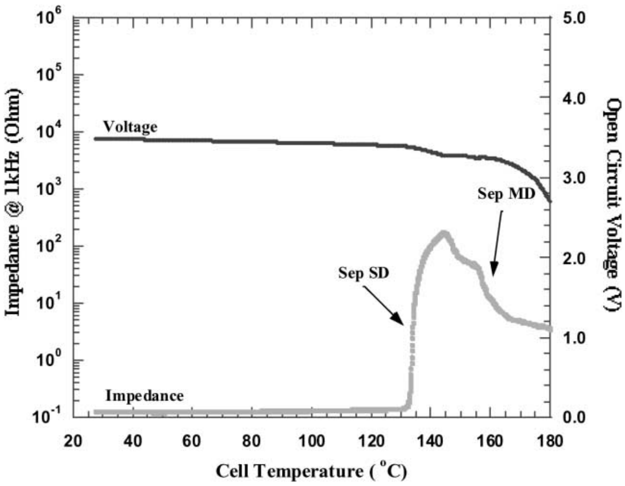

Fig. 2. Impedance and OCV of cell A3 as a function of temperature.

3.1. Shutdown characteristics

Fig. 2 shows the plot of impedance and OCV as a function of cell temperature for cell A3. Due to the lead resistance associated with the experimental setup described in Fig. 1, the impedance value for the cell at ambient temperature was higher than the 49 mΩ listed in Table 2. Increasing cell temperature from ambient to about 130°C resulted in a very small (<20 mΩ) increase in the impedance value. At around 132°C the impedance value increased sharply by over three orders of magnitude. This sharp increase in impedance is due to a separator shutdown (Sep SD) mechanism in the microporous separator membrane present in the Li-ion cell [5]. The observation that shutdown occurs at around 130°C points to the presence of a polyethylene separator in cell A3. This was confirmed by differential scanning calorimetry (DSC) and Fourier-transform infrared spectroscopy (FT-IR). The DSC scan for the separator extracted from cell A3 is shown in Fig. 3a and gives a peak melting temperature of 130°C. The shutdown temperature of a separator is governed by the melting point of the separator material. At the melting point the pores in the separator collapse to the form a relatively non-porous film between the anode and the cathode. The insulating film drastically reduces ion transport between anode and cathode, thereby creating an increase in cell impedance [6].

The impedance of cell A3 (Fig. 2) reached a maximum at around 145°C. At temperatures above 145°C the impedance dropped back down by more than one order of magnitude. This behavior too is typical of polyethylene separators and is indicative of separator meltdown (Sep MD). Separator meltdown is caused by the deterioration of the mechanical properties of the separator material and usually happens at temperatures that are well above the melting point. The drop in impedance may be due to the formation of pinholes in an otherwise non-porous polyethylene film. The impedance–temperature characteristics for cell B were very similar to that observed in cell A3 indicating that cell B too relies on a polyethylene separator to provide shutdown characteristics.

The OCV of cell A3 dropped from around 3.5 V at ambient to around 2.7 V at 180°C. The fact that a significant OCV is registered above 130°C indicates that a finite amount of current can pass through the separator even after shutdown. The observed drop in OCV above the shutdown temperature is difficult to explain and may be due to one or more of the following reasons: (i) temperature induced changes in the active electrode materials; (ii) formation of microshorts in the separator layer and (iii) changes in the electrolyte composition.

Fig. 4 shows the temperature dependence of the OCV and impedance of C2. The shutdown temperature for this cell was at around 135°C, a couple of degrees higher than what was observed for cell A3. Separator meltdown began at around 162°C, at least 15° higher than what was observed cell A3. The difference in the meltdown behavior of the two cells can be attributed to the difference in the construction of the separators in the two cells as is explained below.

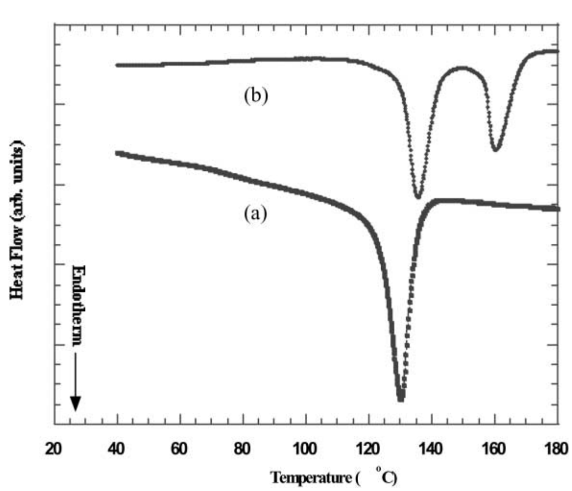

Fig. 3. DSC scans for separators extracted from cells A3 (a) and C2 (b).

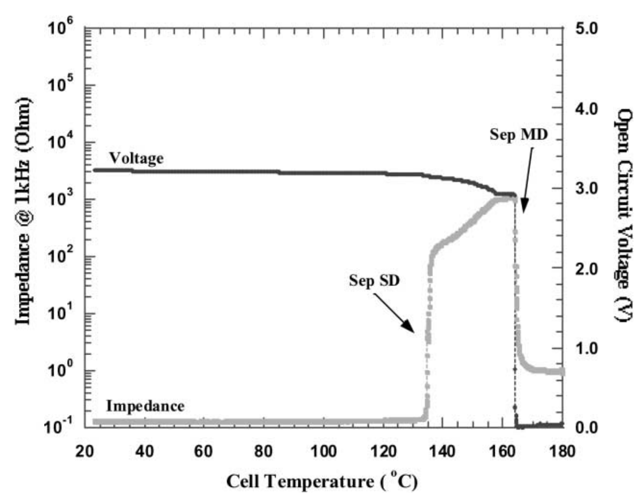

Fig. 4. Impedance and OCV of cell C2 as a function of temperature.

Fig. 3b shows the DSC scan for the separator that was removed from cell C2 and is representative of a polypropylene (PP)/polyethylene (PE)/polypropylene (PP) tri-layer separator. The polyethylene layer had a melting point of 135°C, which is responsible for the shutdown. The polypropylene layer melted at 160°C. The presence of the higher melting polypropylene layer provides the separator with good mechanical properties above the shutdown temperature, thereby providing a higher meltdown temperature. After meltdown, however, the mechanical properties of this separator deteriorated dramatically, as is evident from the sharp and large drop in impedance. The fact that the voltage of the cell at this point is zero suggests that the pinholes created in the separator at meltdown are large enough to create an internal short.

Early versions of Li-ion cylindrical cells primarily used polypropylene single layer separators [7]. However, most of the prismatic Li-ion cells manufactured today either contain a PE single layer or a PP/PE/PP tri-layer separator. Since polyethylene has a lower melting temperature than polypropylene-, polyethylene-based separators offer lower shutdown temperatures. Overcharging studies on some Li-ion cells with re-enforced gel electrolytes have demonstrated the advantages of using a PE-based tri-layer separator instead of a PP separator [8].

The data presented earlier points out at least two major drawbacks of shutdown separators. First, like most other thermally activated cut-off devices the separator shutdown effect is irreversible. While this may not be a serious problem for PE-based membranes, it will be a nuisance if separators with shutdown temperature much lower than 130°C were to be invented. Second, in almost all cases separators are not able to shut the cell down completely. Therefore, an overcharged cell could continue to charge at lower currents even after the shutdown event, rendering the cell a potential hazard if not disposed immediately and safely. Cell manufacturers have addressed this issue by including multiple cut-off devices within a single cell as is discussed below.

3.2. Current limiting characteristics

Fig. 5 shows the temperature dependence of impedance and OCV for cell A2. The impedance for this cell increased gradually starting from about 60°C and is quite unlike the sharp increase that was observed in cell A3. The rate of change in impedance increased with temperature and was maximum at around 125°C. This kind of behavior is characteristic of a positive temperature co-efficient (of resistance) device [4] commonly referred to as the positive-temperature-coefficient (PTC) device. As the name suggests, the resistance of a PTC device increases with increase in temperature. In the case of cell A2, the PTC device is attached external to the cell. It is this PTC device that distinguishes cell A2 from cell A3.

The active component in a PTC device is a highly filled composite of conductive filler and polymer binder.

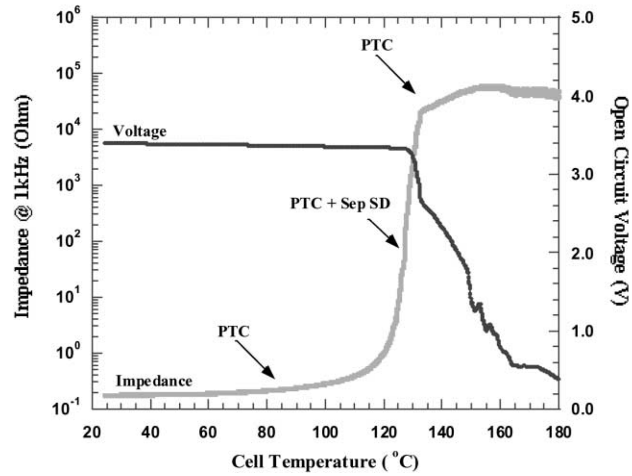

Fig. 5. Impedance and OCV of cell A2 as a function of temperature.

Temperature induced expansion of the polymer binder leads to an increase in the resistance of the composite. These changes take place over a wide temperature range. So, unlike shutdown separators, PTC devices respond with a change in impedance over a wider temperature range. The biggest and sharpest increment in impedance at around 125°C is associated with the melting point of the polymer binder and is almost indistinguishable from the separator shutdown event that takes place in this cell.

Fig. 6 shows how the impedance of a PTC device removed from cell A2 changes with temperature. Ideally, a PTC device is expected to perform reversibly. In this case however, cooling data could not be collected because of a failure in the joint between the PTC and the battery tab. The failure was associated with a conductive adhesive that was used to attach the PTC device to the tab. It is also possible that the any impedance changes that took place in this conductive adhesive during the experiment are reflected in the impedance curves in Figs. 5 and 6. No attempt was made to re-tab

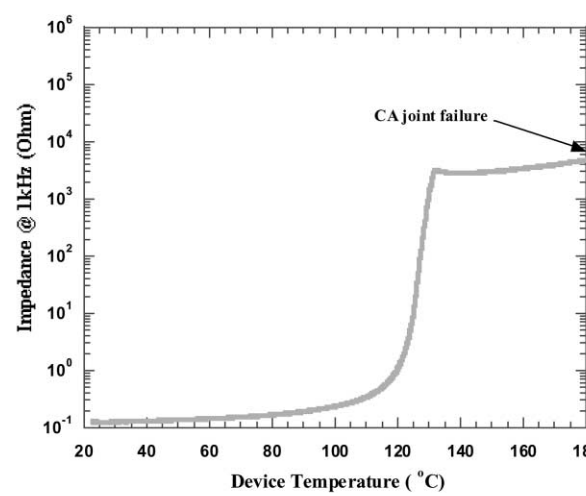

Fig. 6. Impedance of a PTC device extracted from cell A2 plotted as a function of temperature.

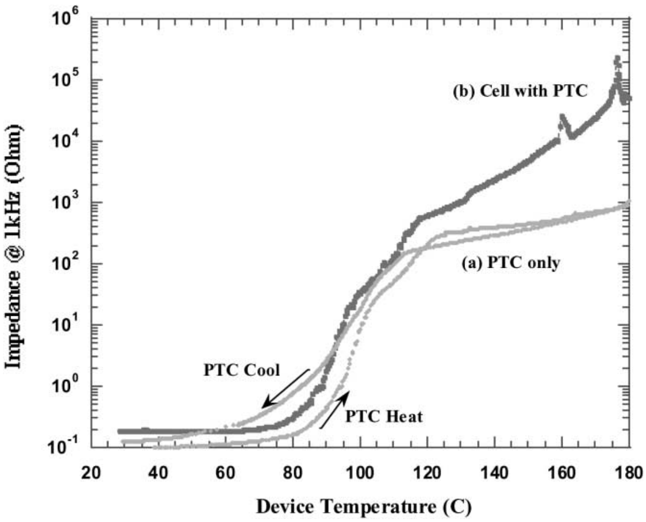

Fig. 7. Impedance–temperature relationship for: (a) PTC device extracted from cell C1 and (b) cell C1 with PTC device.

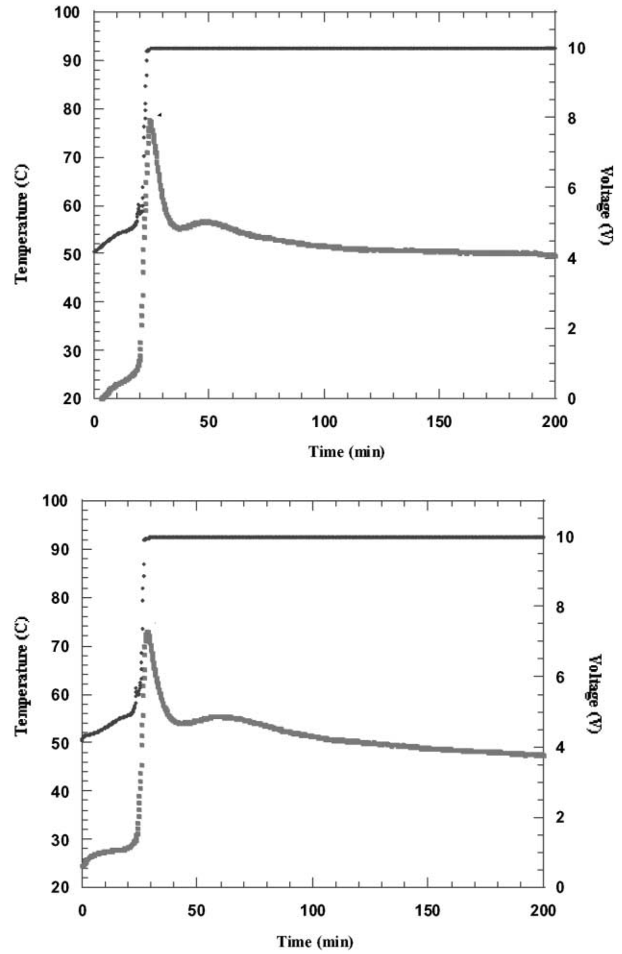

Fig. 8. Overcharge data for cell A1: (a) without PTC device and (b) with PTC device.

the device because of concerns that this action may lead to a change in the properties of the active material contained in the PTC.

The reversible nature of a PTC device removed from another cell, C1, is demonstrated in the impedance–temperature curve in Fig. 7a. This device was attached to tabs using solder that withstood the highest temperature in the experiment. The small hysteresis in the curve is probably due to irreversible temperature-induced structural changes in the polymer matrix. The combined effect of the PTC device and the shutdown separator on the impedance–temperature relationship of cell C1 is shown in Fig. 7b. The spike at 160°C is associated with the melting of the polypropylene in the tri-layer separator that is present inside this cell (see Fig. 10b). The spike at around 175°C is probably attributable to the melting of the solder that was used to attach the PTC to the tab.

PTC devices are current limiting devices. Excess current passing through the device generates heat due to resistive heating and raises the impedance of the active layer. When this happens, the amount of current flowing through the device is automatically reduced. This current limiting mechanism makes the PTC device ideal for preventing or reducing the damage caused by an external short. The current-limiting capability and the activation temperature of a PTC device can be tailored by judicious selection of the materials that go into the active layer and also by optimizing the dimensions. The PTC devices that are used in prismatic cells had impedance values between 20 and 50 mΩ. This raises the impedance of the cell significantly and may make it unattractive for certain applications that are very sensitive to the impedance value of the energy source.

External PTC devices like the ones found in cell C1 and cell A2 are not effective in preventing overcharge. Even when the internal cell temperature is around 130°C the skin temperature of the cell may not be high enough to activate the PTC. Hence, the impedance of the PTC device is not high enough to make a difference. In such cases, the shutdown separator is more responsive to an overcharge situation since it is an integral part of cell. This is certainly the case with cell A1. Overcharge experiments for two charged cells, one with and the other without a PTC device, yielded identical results — cell shutdown after around 26 min with a maximum skin temperature of around 75°C — as shown in Fig. 8a and b. Charging was done at 1.5 A using a 10 V power supply. The impedance–temperature behavior of cell A1 was found to be similar to the behavior demonstrated by cell A2, as was confirmed in a separate experiment.

Most cylindrical cells are designed to have PTC devices internal to the cell and are expected to be more responsive in an overcharge situation. The device is usually integrated into the cell's header. Only one of the prismatic cells studied in this work, cell D2, had an internal PTC device. The internal PTC is responsible for the impedance jump that takes place at around 105°C in the impedance–temperature curve in Fig. 9. The impedance increase due to the activation of the PTC is only one order of magnitude, much lower than what

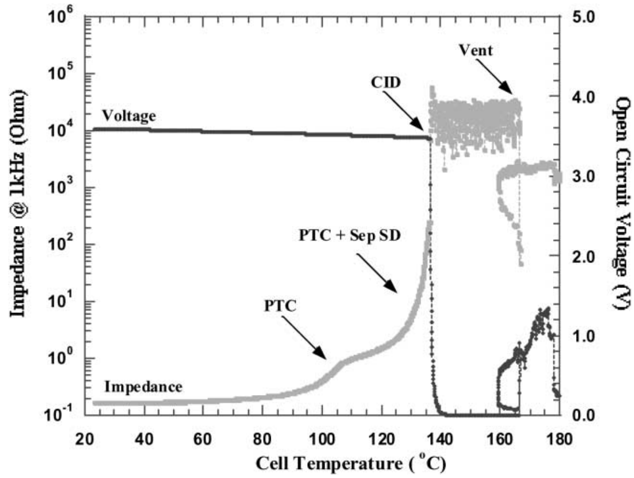

Fig. 9. Impedance and OCV of cell D2 plotted as a function of temperature.

was observed for cells with the external PTC. This may be due to a difference in the design of the PTCs used.

3.2.1. Circuit breaking characteristics

The impedance–temperature relationship for cell D2, shown in Fig. 9, is more complex than what was observed for the cells discussed previously. As was mentioned earlier, cell D2 is the only prismatic cell in the group studied here that has an internal PTC device. This device is responsible for the increase in the impedance of the cell up to around 115°C. The sharp rise in the impedance value observed between 125 and 135°C can be attributed to the shutdown of the polyethylene separator present in the cell. This event is followed at around 135°C by yet another rapid increase in impedance measuring at least two orders of magnitude. The OCV of the cell also dropped sharply to zero at this temperature and is indicative of a circuit breaker mechanism. Reverse engineering of the cell confirmed the presence of a current interrupt device (CID). Indirectly, a CID can be activated by high temperature. Increase in the temperature inside the cell causes an increase in the vapor pressure of the non-aqueous electrolyte solvent, triggering a break in the contact between jelly — roll and the header assembly. The circuit-breaker mechanism that is provided by the CID is widely used in cylindrical Li-ion batteries [7]. The erratic impedance data in the temperature range 140–160°C in Fig. 9 may be occurring because the CID has not detached cleanly and completely from the jelly-roll.

A fourth event was also observed in cell D2 at around 170°C. This event was marked by a slight decrease in the impedance and a slight recovery of the OCV. Both of these changes are also accompanied by a decrease in the cell temperature by about 5°. This event is attributed to a cell venting mechanism. Most Li-ion cells have a venting mechanism built into the can. Like the CID, vents are activated when the vapor pressure of the electrolyte exceeds a certain critical value. If the venting process results in the expulsion of a significant amount of electrolyte, as is the case with cell D2, the cell may experience a temporary cooling effect. Although most of the cells studied had vents, cell D2 was the only one that demonstrated this cooling effect. Others either failed to vent or vented with only a small loss in the electrolyte. It is important to emphasize here that these studies were carried out on discharged cells. Charged cells usually contain more reactive electrodes and their reactions with the electrolytes may lead to venting at lower temperatures. Cell D1 showed impedance–temperature characteristics similar in most respects to that observed in cell D2. It did not, however, demonstrate any significant increase in impedance value below the shutdown temperature of the cell — indicating that no internal PTC device was included with cell D1.

Fig. 10 shows the impedance–temperature relationships for an ‘‘as received’’ cell C1 and the same cell with all the external safety components removed. As was discussed earlier, cell C1 had an external PTC device that can account for the small increase in impedance values observed below 90°C. At 90°C the impedance value of the cell shot up to infinity. The OCV of the cell at this temperature was 0 V. This irreversible, cut-off feature was provided by an external thermal fuse [4]. The active element in the thermal fuse is an alloy that has a sharp and well-defined melting point. These devices come in a variety of shapes and form factors and are used widely in electrical and electronic products that are inclined to heat up during use. One of the drawbacks associated with thermal fuses is the fact that they are irreversible. Care must be taken to assure that the thermal fuse is not activated during assembly in cell or during accelerated life testing cycles.

The impedance–temperature relationship of cell C1 without the external safety devices is also shown in Fig. 10. The curve is very similar to the one observed for cell C2 and is indicative of a shutdown separator.

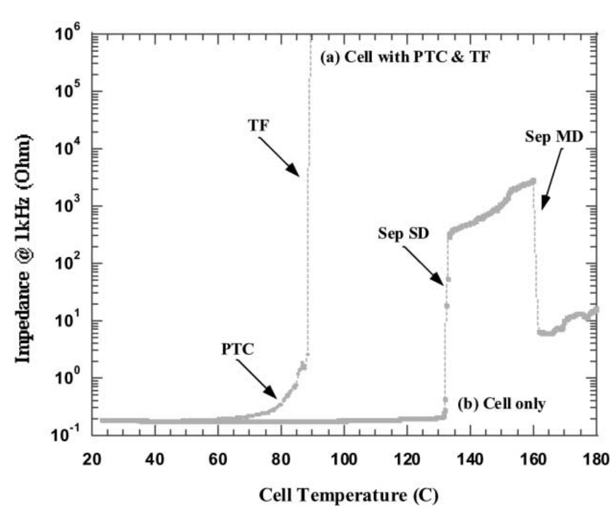

Fig. 10. Impedance–temperature relationship for: (a) cell C1with external PTC device and thermal fuse and (b) cell C1 without any external devices.

In addition to the safety component discussed in this manuscript, Li-ion cell researchers are investigating a variety of alternative approaches to make cells safer for use. It is possible that some of these mechanisms were already present in the cells used in this study but were not detected by merely monitoring impedance–temperature and OCV–temperature behavior. For example, the electrolyte in a Li-ion cell may contain additives that promote gas generation under certain conditions. The gas that is generated may help in the activation of the vent and/or the CID. Other studies have focused on designing electrolytes that may be cross-linked at elevated temperatures, thereby increasing the impedance of the cell just enough to prevent catastrophic failure. In parallel with all the R&D in safety mechanisms, research groups are also attacking the root cause by trying to identify and synthesize electrodes and electrolytes materials that are less reactive than the ones used today. However, there is also a never-ending demand for materials that have higher energy density and higher rate capability. Finding a single set of components that can meet both the performance and safety requirement is a very challenging task.

4. Conclusions

The mechanism and characteristics of thermal cut-off devices in several prismatic Li-ion cells were studied by monitoring the impedance (Z) at 1 kHz and the OCV of the cells as a function of temperature. Increase in cell impedance due to the PTC device occurred gradually over the temperature range 60–125°C. The rate of change in impedance increased as a function of temperature and for the cells used in this study, reached a maximum somewhere between 95 and 120°C. Above 125°C, the effect of the PTC is combined with that of the shutdown separator. All the cells studied contained polyethylene-based microporous separators with a shutdown temperature between 130 and 135°C. Within this narrow temperature range, the shutdown separator caused a sharp (around three orders of magnitude) and irreversible rise in impedance of the cell. Single layer PE separators were effective up to around 145°C, above which they demonstrated a meltdown effect. Tri-layer separators had meltdown temperatures as high as 160°C because of the presence of additional layers of higher melting polypropylene. Irreversible cut-off could also be provided by a current interrupt device or a thermal fuse, with the latter typically being activated irreversibly well before the SD separator at around 90°C. Both, the thermal fuse and the CID had a circuit-breaker effect, causing the OCV of the cell to drop to zero. The CID was activated at around 140°C for an uncharged cell. Other thermally activated events such as cell venting and weld/joint failure also contributed to changes in impedance and OCV and could also be studied by monitoring their behavior as a function of temperature.

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