Safety Performance for Phosphate Based Large Format Lithium-Ion Battery

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***Abstract* - The use of lithium-ion batteries in many of today's electronic consumer products has increased significantly due to the advantages of high energy density, high cell voltage, and longer shelf life over that of comparable battery chemistries. The cell chemistry of conventional lithium-ion batteries has been limited by the choice of suitable lithium liberating cathode materials i.e. the three oxide electro active materials: $LiMn_2O_4$, $LiCoO_2$ and $LiNiO_2$ (Lithium-Manganese, Lithium-Cobalt, and Lithium-Nickel respectively). These materials are generally found to offer high electrochemical performance at the expense of poor thermal stability. The three lithium oxide's thermal instability when over-charged has limited the application of these materials to small and relatively low capacity lithium-ion batteries. The novel use of a phosphate-based material in the cathode has been found to offer many of the advantages of traditional lithium-ion chemistries without sacrificing the safety necessary in a large format application.**

In this paper, the results of safety testing comparing phosphate-based cells and the most popular of the three lithium oxide materials (lithium-cobalt), will be presented. Test data will show that the safety circuitry used in popular lithium-cobalt 18650 cylindrical cells will not prevent an event or propagation of an event if thermal runaway occurs within one cell in a battery pack. In contrast, abuse testing of phosphates based cells shows no thermal events under identical conditions.

I. Introduction

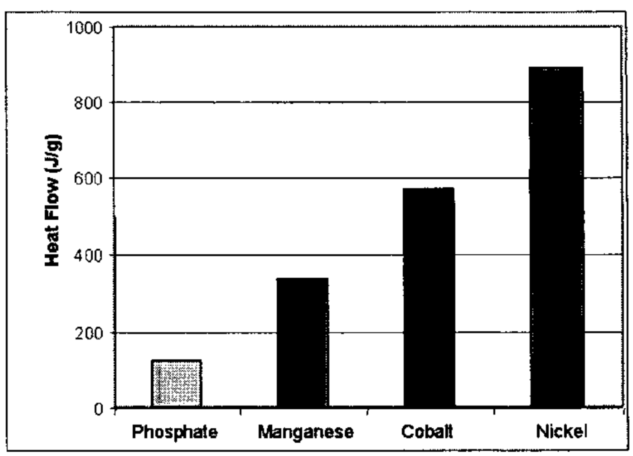
Designing large format power systems using traditional lithium-ion technology has been a great challenge when considering the concerns regarding the toxicity, sensitivity to over-charge, over-discharge and thermal runaway associated with the three traditional lithium oxide chemistries. These problems have been virtually eliminated by using a phosphate based lithium-ion chemistry, comprised of environmentally friendly materials. Using a phosphate cathode material in a battery cell allows a thermally stable and environmentally friendly cell without the use of toxic metals. Phosphate based lithium-ion batteries retain the outstanding cycle life of lithium-ion cobalt in large capacity batteries without compromising safety due to the inherent safety properties of phosphate based cathode materials. By developing a safer alternative, large format opportunities in markets like HEV, telecom and electric utility, can be realized with lithium-ion technology.

Various protection mechanisms are often employed with lithium-ion power systems. They range from internal cell safety separators to fuses, contactors, and carefully controlled charging algorithms and monitoring. However, the need for an inherently safe chemistry is needed when batteries are subjected to harsh conditions or when they are placed in sensitive areas. Abuse conditions can always occur and can subject a battery to a condition in which the various safety mechanisms may not be able to prevent a thermal event.

II. Inherent Safety of Phosphates

The thermal instability of lithium-cobalt is directly related to the ease of liberating oxygen in $LiCoO_2$. This oxide bond is relatively weak and can be broken at relatively low temperatures. In the case of a thermal runaway situation, the oxygen being released by a lithium-cobalt cell provides fuel to the exothermic reaction when the electrolyte is decomposing due to an overcharge. Hence upon abuse, a lithium-cobalt cell will continue to burn until its oxygen supply is gone.

FIGURE 1
PHOSPHATE HAS LOWEST HEAT FLOW



On the other hand, $LiFePO_4$ has extremely strong oxygen bonds with P^{5+}, resulting in a very stable oxygen structure. Lithium-phosphate does not easily liberate oxygen, thereby providing a much more thermally stable battery cell.

Differential Scanning Calorimetry (DSC) provides a method of determining thermal stability. A controlled temperature rise is induced and the subsequent heat generated

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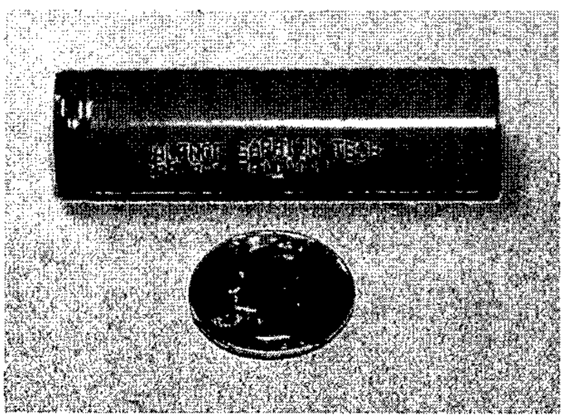
by the different cathode materials is measured. The exothermic heat flow of each cathode material is shown in FIGURE 1, which shows phosphate's inherent thermal stability. The lower the heat flow, the higher tolerance it has to extremely high temperatures.

III. TESTED CELLS

The lithium-cobalt cell tested is an ICR18650-type, obtained by removing the cylindrical cells from common off the shelf notebook computer battery packs. This lithium-cobalt cell is denoted as an "Oxide18650" in all figures. Comparison testing was done against a similar cylindrical cell with a phosphate based cathode material. All cells have internal PTC safety separator devices.

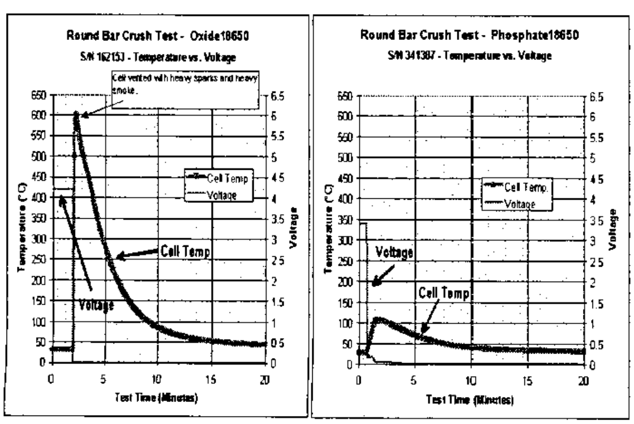
FIGURE 2
VALENCE SAPHION 18650 CELL



IV. ROUND BAR CRUSH TEST

The round bar, slow crush test creates an internal short inside a battery cell to mimic common conditions when a battery is damaged from abuse. Sudden impacts and sustained vibration can cause micro-shorts inside a cell and this test seeks to determine what type of event would result when a micro-short occurs.

FIGURE 3
ROUND BAR CRUSH TEST RESULTS



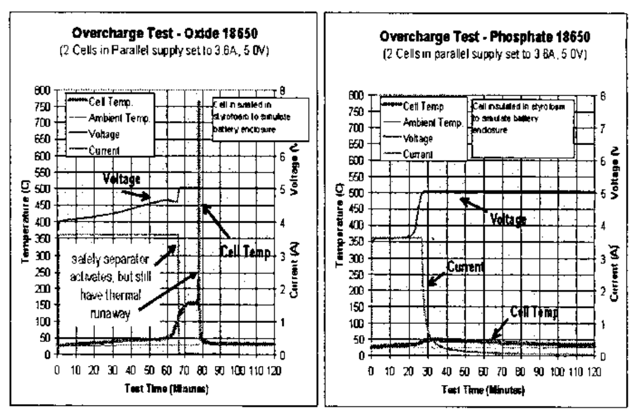
A hydraulic press was used to slowly lower a 6mm diameter round bar perpendicular to the 18650 cylindrical cell. The round bar was stopped once the open circuit voltage dropped abruptly or an event occurred. The speed of the crush is important to determining the event resulting from a short. A quick crush can sometimes effectively smother a cell, while a slow crush can effectively induce the short. The lithium-cobalt cell failed by jetting heavy sparks along with thick smoke. The end caps of some cells would also be forcefully blown off with a loud bang, expelling the entire contents of the cell. The left graph in FIGURE 3 shows that the cell temperature rose to over 600°C with an instant drop in voltage. Even 3 minutes after the thermal event, the cell temperature remained over 250°C showing the extreme exothermic reaction of lithium-cobalt.

The lithium-phosphate cell on the other hand exhibited an extremely benign event upon being shorted. The cell voltage drops quickly, yet the cell temperature rises to only 110°C. The low heat flow characteristic of lithium-phosphate is confirmed in this test.

V. 5V OVERCHARGE TEST

Lithium-cobalt cells are generally unstable in an overcharge condition. Great care goes into the cell protection circuitry and proper charging profiles and monitoring. However, a malfunctioning charger, inappropriately sized charger, or user error can easily overcharge a battery cell. This test seeks to determine how robust a battery cell is to an overcharge condition.

FIGURE 4
OVERCHARGE TEST RESULTS



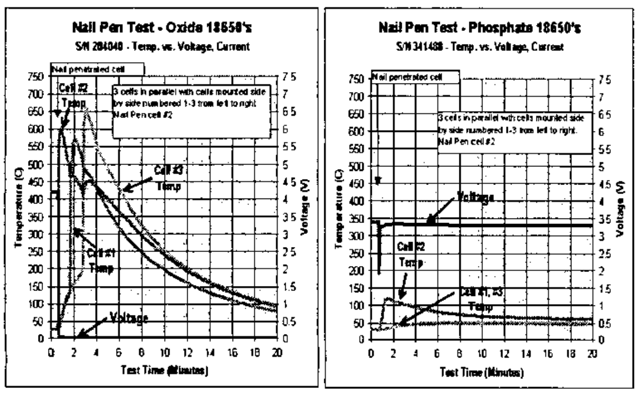
The graph on the left in FIGURE 4 shows a 3.7V nominal lithium-cobalt cell being overcharged by an additional 1.3V. All cells start at a 0% state of charge and the voltage steadily ramps up as shown. Even at 4.2V (0.5V above nominal), the lithium-cobalt cell temperature is already starting to quickly rise. Once the temperature has reached 120°C, the PTC safety separator in the cell activates and the cell current drops to zero as expected. Though the cell temperature seems to stabilize at 155°C, there is enough thermal momentum such that after 12 minutes at 5V, the cell exhibits a sudden thermal event. The temperature spikes up to an incredibly high 750°C and glows red hot until all the oxygen is burned from the cell. Heavy sparks, smoke, and flame are also witnessed.

The lithium-phosphate cell produces very little thermal output upon overcharge. The 3.4V nominal lithium-phosphate cell exhibits a higher percentage overcharge (1.6V above nominal), but still shows no thermal event compared to the lithium-cobalt cell. The graph on the right shows the safety separator activating and the subsequent drop in current of the cell when the overcharge is held at 5V. However, the cell temperature rises to a peak of 55°C and no event is witnessed even after several hours.

VI. Nail Penetration Test

This abuse test shows a typical battery pack of 3 cells in parallel. A nail penetration test represents a severe condition in which a sharp 3mm diameter metal nail punctures a cell. This test also seeks to determine whether a battery pack can maintain its integrity when a single cell has been damaged.

FIGURE 5
NAIL PENETRATION TEST RESULTS

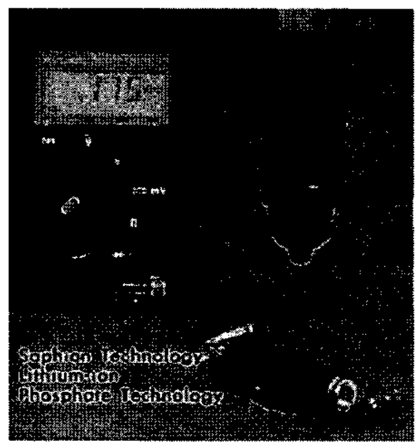


In the lithium-cobalt pack shown in FIGURE 5, a nail is driven through the middle cell, which immediately creates a thermal event in that cell. The lithium-cobalt cell fails with sparks and smoke and by forcefully ejecting the contents of the cell out with a loud bang. Of the cells that fail with heavy sparks, the subsequent spike in temperature to 600°C will cause the neighboring cell to also exhibit a thermal event after one minute. This thermal event propagation occurs regardless of the safety separator in each cell.

FIGURE 6
LITHIUM-ION COBALT OXIDE NAIL PENETRATION

The lithium-phosphate pack on the other hand continues to show the inherent safety of a phosphate based cathode material. The cell temperature of the abused cell does not rise high enough to significantly impact the other cells. In fact, the pack voltage remains at 3.4V and only a loss of capacity is incurred.

FIGURE 7
VALENCE SAPHION NAIL PENETRATION



VII. Summary

Inherent chemical properties of a phosphate structure ensure that oxygen is not easily liberated and therefore will not result in an exothermic reaction when heated. The intrinsic safety of a battery cell is critical when designing battery systems with high energies and used in sensitive areas. External safety devices are not enough to prevent a propagation of events from occurring under abusive conditions. Even in several extremely abusive conditions in which traditional lithium-cobalt cells exhibited sudden thermal events, the lithium-phosphate cell exhibits an extremely benign reaction, proving the viability of a phosphate-based battery in large format applications.