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Assessment of thermal runaway in commercial lithium iron phosphate cells due to overheating in an oven test

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Abstract

Overheating by oven exposure testing is a fundamental method to determine the severity of thermal runaway (TR) in lithium-ion cells. The TR behavior of lithium iron phosphate (LFP) cells under convection oven exposure is quantified and a comparison is made of their stability and severity against that of lithium metal oxide cells under similar conditions presented in the literature. The convection oven test is carried out at 180°C and 220°C, the TR response of the LFP cells is shown to be significantly more stable and less severe than lithium cobalt oxide cells tested in the literature. Also, under an oven abuse test a cylindrical cell is shown to have near uniform surface temperature along its length.

Keywords: Thermal Runaway; Lithium Iron Phosphate Cells; Thermal Abuse; Oven Test; Li-ion

1. Introduction

Due to their high energy density, high cycle life, high efficiency and low self-discharge, lithium-ion rechargeable batteries (LIBs), with their many forms of metal oxides and phosphate cathodes, are a popular energy storage device for portable electronics, electric vehicles and also stationary applications [1–3]. However, LIBs are susceptible to thermal runaway (TR), a dangerous and potentially catastrophic failure of the battery through uncontrollable self-heating due to the exothermic decomposition of the cells major components i.e. the electrodes and electrolyte [4–6].

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As modern applications of energy storage are requiring batteries of greater energy capacity, there in turn is an increased risk to safety, as the critical failure such a battery will present a greater fire and explosion hazard than a lower capacity battery [7].

One way to address the risk of TR is through the selection of cell chemistry within the battery. Cells with a lithium iron phosphate (LFP), $LiFePO_4$, cathode have been shown to be the most stable and result in the least severe TR events [8–13]. This is believed to be due to the inhibition of O_2 from the cathode, due the strong covalent bonds between the phosphorus and oxygen of the $LiFePO_4$ active material, which in turn limits the amount of O_2 available to react with electrolyte and hence reduces the overall heat produced [8]. Despite this fact making them highly suited for large format Li-ion batteries [13], LFP cells have not been studied under oven test conditions like lithium metal oxide based cells.

Convection oven tests can provide crucial data on the response of a cell exposed to high temperatures, which may occur because of high ambient temperatures due to operational environment or failure of the cooling system, or due to a neighbouring cell in a pack failing by other means and going into TR. Tests of this nature have been carried out under free [14,15] and forced [16] convection, *Tobishima and Yamaki* [14] used thermal ramping to heat the cell up from ambient to a desired oven temperature, while *Hatchard et al.* [15] lowered cells into a preheated oven. They both show, for cells with metal oxide based cathodes, that at higher oven temperatures TR occurs sooner and is more severe, i.e. results in higher cell temperatures. *Tobishima and Yamaki* [14] also shows that a small increase in oven temperature, from 150°C to 155°C, can result in the difference between no TR and TR occurring in an extreme manner. *Golubkov et al* [9] shows that under adiabatic like conditions with constant power supplied to a heater placed around an 18650 LFP cell at 100% SOC the cell reaches a maximum temperature between 400°C-450°C during TR.

This paper aims to quantify the TR response of LFP cells under oven exposure and compare their stability and severity against that of lithium metal oxide cells under similar conditions presented in the literature. The remainder of the paper presents the methodology of the convection oven exposure test, the results and discussion of this test and finally the concluding remarks.

2. Methodology

Commercial *ENIX Energies* 1500 mA h cylindrical 18650 $LiFePO_4$ cells were chosen as a case study to undergo overheating in an oven test. The cells are rated at a nominal voltage of 3.2 V and a max voltage of 3.65 V. The oven test was carried out on cells charged to 100% SOC at oven set temperature of 180°C and 220°C. The LFP cells were charged on a *MACCOR 4000M* battery cycler using a constant current – constant voltage (CC – CV) method. With CC charge criteria of 0.5C (cut off: voltage > 3.65 V) and CV criteria of 3.65 V (cut off: current < 0.01C). A *VWR DRY-Line 53* natural convection oven (internal dimensions 401×401×330 mm) was used to perform the oven tests, where a steel wire shelf at a central height inside the oven was used for the support of cells. The oven was heated to the required abuse temperature before a cell was placed centrally on the shelf inside the oven to ensure the cell was heated evenly on all sides. The temperature of the cell and oven were measured with K-type thermocouples linked to a *Pico USB- TC-08* data logger and PC to record the data. Fig. 1 shows a schematic of the experimental setup including the placement of the thermocouples. The thermocouples were attached to the cell 1cm away from the terminal using glass cloth tape, while the cell had its shrink wrapping removed to improve the contact between cell and thermocouples. The oven thermocouple was place away from the cell and out of the path of vented gasses to minimize any affect the heating from the cell or gas jet would have on the oven temperature reading. At the instant of placing the cell in the heated oven, the temperatures were recorded for the following 90 min.

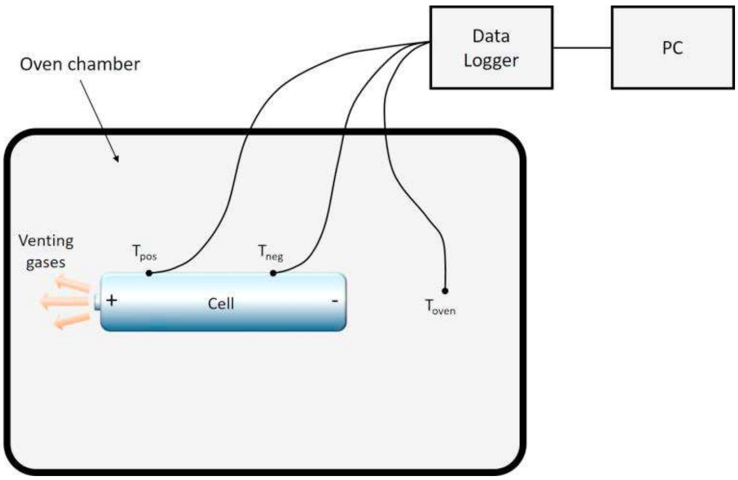

Fig. 1. Schematic of oven abuse test set up (T_x represent the placement of thermocouples).

3. Results and Discussion

Fig. 2 shows the cell surface temperature at both the negative and positive ends of the cell, and also the oven temperature for the oven set temperatures of 180°C and 220°C. It can be seen form Fig. 2 that at the start of the test there is a drop in oven temperature. This was caused by the need to open the oven to inset the cell. However, as the temperature of the oven before TR has occurred is the factor that will affect the response of the cell, one can take the average oven temperature up until the cell maximum temperature as the oven temperature for comparison between tests. In this manner, the 180°C and 200°C test cases have average oven temperatures of 170°C and 210°C respectively.

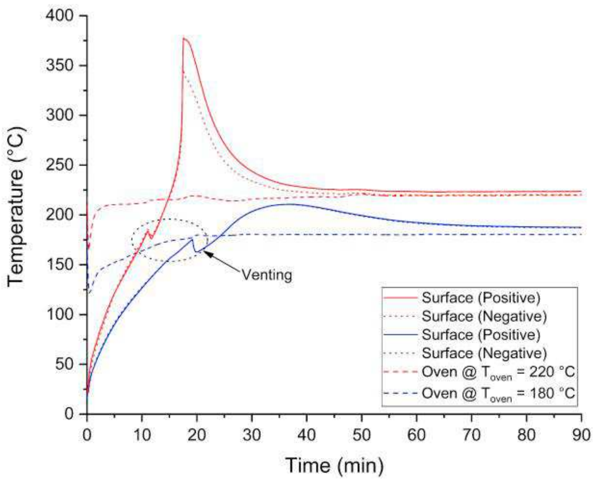

Fig. 2. Cell surface and oven temperatures for oven set temperatures of (red) 220°C and (blue) 180°C.

The surface temperature profiles in Fig. 2 show that in the 180°C case there is negligible temperature difference between the two thermocouples. This is true even when venting occurs at the positive terminal, cooling the cell due to the pressurized gases in the cell expanding in the open atmosphere as they are expelled from the cell. The uniform temperature over the cells surface is due to the high axial thermal conductivity of the steel cell can and copper and aluminum jelly roll windings. In the 220°C case the temperature reading of the negative terminal thermocouple is significantly lower than the positive terminal thermocouple. However, on analysis of the cell after it was removed from the oven, it was discovered that the negative terminal thermocouple was no longer in direct contact with the cell surface, and hence was not recording the true surface temperature. As such, it can be assumed if the negative terminal thermocouple was properly attached, that both thermocouples would read similar values to each other, as in the lower temperature case. Following this, we can state that, under uniform heating the cell has a near uniform surface temperature along its length before, during and after TR.

Comparing the surface temperature profiles in Fig. 2, it can be seen that at the higher oven temperature TR occurs 1) sooner, due to the increased convective heat transfer from the air to the cell, and 2) to a greater severity, shown by the increased maximum cell surface temperature and increased cell surface temperature rate. We attribute the increased severity of the test at 220°C oven set temperature over the 180°C oven set temperature to the occurrence of the electrolyte reaction at in the 220°C. *Chen & Richardson* [8] state the highly energetic electrolyte reaction occurs at temperatures above 250°C. Hence, in the 180°C case where the maximum cell surface temperature does not reach above 211°C, it can be assumed the internal cell temperature does not reach the point for the onset of the electrolyte reaction, while in the 220°C it can be seen that the surface temperature profile becomes steeper at approximately 245°C -255°C indicating the electrolyte reaction is taking place.

Inspecting the critical oven temperature to induce rapid TR and the maximum cell temperature during TR of the LFP cells tested here to that of lithium cobalt oxide (LCO) cells tested by *Tobishima & Yamaki* [14] and *Hatchard et al.* [15], a comparison can be made between the stability and severity of the two types of chemistries. These quantities show that LFP cells are more stable, going into rapid TR at oven temperatures between 170°C-210°C rather than at 155°C in the case of LCO cells. LFP cells also have a less severe TR event. At an average oven temperature of 170°C they reach a maximum temperature of less than 400°C, while LCO cells reach temperatures above 700°C at 155°C oven temperatures.

As the safety of a battery pack is directly related to the safety of the cells that the pack is constructed of, then the use of LFP cells, such as the cells that these findings have shown to be a safer alternative to LCO cells, will in turn improve the safety of a battery pack. This supports the suggestion by *MacNeil et al* [13] that LFP cell are suited to large format batteries, which have a greater energy capacity and hence safety is a greater concern, especially batteries that would be use in a domestic setting were risk to people is greater or in harsh environments where the probability of abuse is greater.

4. Conclusion

The TR response of LFP cells was investigated by overheating in a convection oven. Cells placed in ovens at higher temperature went in to TR sooner and to a greater extent. At an oven set temperature between 180°C-220°C the cells went from a mild TR event to a significant TR event, due to cells in the 220°C oven set temperature case reaching a temperature that lead to the onset of the electrolyte. In comparison to LCO cells under oven test in the literature, TR events in LFP cells are much more stable and less severe.

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