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Cathode material comparison of thermal runaway behavior of Li-ion cells at different state of charges including over charge

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HIGHLIGHTS

- Accelerating rate calorimetry measurements were carried out using 18650 Li-ion cells.
- Thermal runaway behavior of $LiCoO_2$ and $LiMn_2O_4$ cathode materials are compared.
- Thermal mapping at different SOCs including overcharge was obtained.
- OCV and internal resistance of Li-ion cells were monitored during ARC measurements.

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ABSTRACT

The analysis of Li-ion secondary cells under outstanding conditions, as overcharge and high temperatures, is important to determine thermal abuse characteristics of electroactive materials and precise risk assessments on Li-ion cells. In this work, the thermal runaway behavior of $LiCoO_2$ and $LiMn_2O_4$ cathode materials were compared at different state of charges (SOCs), including overcharge, by carrying out accelerating rate calorimetry (ARC) measurements using 18650 Li-ion cells. Onset temperatures of self-heating reactions and thermal runaway behavior were identified, and by using these onset points thermal mapping plots were made. We were able to identify non-self-heating, self-heating and thermal runaway regions as a function of state of charge and temperature. The cell using $LiMn_2O_4$ cathode material was found to be more thermally stable than the cell using $LiCoO_2$. In parallel with the ARC measurements, the electrochemical behavior of the cells was monitored by measuring the OCV and internal resistance of the cells. The electrochemical behavior of the cells showed a slightly dependency on SOC.

1. Introduction

The use of Li-ion cells has been growing globally with a large number of cells powering a wide range of applications in different environments, and there have been several reported incidents raising safety concerns. Some of the cases have been related to overheating (thermal runaway) of Li-ion cells, leading to possible fire and explosion. The thermal behavior of a Li-ion cell is dominated by the exothermic reactions between the electrolyte and electroactive materials [1–3]. Thermal runaway occurs when the exothermic reactions go out of control, thus the self-heating rate of the cell increases to the point that it begins to generate more heat than what can be dissipated [4,5].

There are safety concerns related to the upsizing of Li-ion cells and the use of oxide based cathode materials, since oxygen release from the cathode material at high temperatures can accelerate the combustion reactions in the cell driving its components into fire or explosion. Therefore, the thermal analysis of complete Li-ion secondary cells is important for ensuring their safety and reliability.

The use of accelerating rate calorimetry (ARC) allows the thermal analysis of Li-ion cells. Many researchers have investigated the thermal behavior of different cathode materials in contact with different solvents and electrolytes using ARC [2,3,5–9], however, a

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few results on the thermal behavior using complete Li-ion cells have been reported.

There are a few investigations on the thermal behavior of complete Li-ion cells [10,11], and the analysis of cathode electroactive materials under outstanding conditions, as overcharge and high temperatures, is important to determine thermal abuse characteristics of electroactive materials and precise risk assessments on Li-ion cells. In this work, we compare the thermal runaway behavior of two widely used cathode materials in commercial Li-ion cells, $LiCoO_2$ (LCO) and $LiMn_2O_4$ (LMO), at different state of charges including overcharge (120% SOC), using 18650 Li-ion cells and carrying out ARC measurements. In parallel with the ARC measurements, the internal resistance and open circuit voltage (OCV) of the cells were monitored. We were able to identify non-self-heating, self-heating and thermal runaway regions of LCO and LMO cells as a function of state of charge and temperature.

2. Experimental

2.1. Li-ion cell specifications

Two types of commercial 18650 Li-ion cells with different cathode materials were used in this work. The first type used $LiCoO_2$ as cathode active material and graphite as anode active material (LCO-Graphite cell). The second type used $LiMn_2O_4$ (LMO) as cathode active material and graphite as anode active material (LMO-Graphite cell). The electrolyte consisted of a solution of 1 M of $LiPF_6$ in ethylene carbonate and dimethyl carbonate (1:1, w/w). The information of the composition of electroactive materials and electrolyte was taken from the corresponding Li-ion cell data sheet. The capacity of LCO-Graphite cell was 800 mAh and the capacity of the LMO-Graphite cell was 720 mAh.

2.2. Accelerating rate calorimetry

Before carrying out the ARC measurements, the cells were charged to the desired state of charge using a battery tester (KIKUSUI, PFX2011). Thermal runaway tests were carried out using an accelerating rate calorimeter (ARC) 2000™ Columbia Scientific Industries. The cells were set to the desired SOC and placed inside the ARC cavity. We considered that a cell is full charged, 100% SOC, when this is charged to 4.1 V (defined by the cell manufacturer), using a charging current of 0.2C and following a constant current–constant voltage (CC–CV) process, Fig. 1. To set the cells to the desired SOC, the cells were fully charged and then discharged to the corresponding SOC using a discharging current of 0.2C following a constant current (CC) process. In the case of 120% SOC, the cells were fully charged to obtain their charging capacity, and then they were charged 20% according to the charging capacity obtained.

To record the temperature of the cell, a thermocouple was placed on the surface of this. The calorimetry measurements were conducted following a Heat-Wait-Search method. During the heat-step, the cell is heated in periods of 5 °C follow by a waiting-step of 30 min and a searching-step of 5 min. If during the searching-step, a self-heating with a heating rate higher than 0.05 °C min^{-1} is detected, the calorimeter shifts to adiabatic mode and tracks the cell temperature until the end the self-heating reaction. If no self-heating is detected, the next heat-step is immediately initiated. The thermal runaway measurements were carried out until surface of the cell reached a temperature of 200 °C. The ARC measurements were carried out at 0%, 25%, 50%, 75%, 100% and 120% SOC.

In parallel with the ARC measurements, the internal resistance at 1 kHz and the OCV of the cells were recorded using a milliohmmeter (Agilent 4338B) and a multimeter (Keithley 2100), respectively.

3. Results and discussion

Fig. 2 shows the thermal behavior of the LCO-Graphite cell during the ARC measurements at 0%, 25%, 50%, 75%, 100% and 120% SOCs. A temperature drop is observed at some SOCs, this drop in temperature is likely due to the volatilization of the electrolyte. A temperature drop is not observed when the heat generated by the cells is larger than the heat released by the volatilization of the electrolyte. Table 1 shows the onset temperatures of self-heating and thermal runway reactions of LCO-Graphite cell at different SOCs. The onset temperatures decrease by increasing the state of charge. The differences of the onset temperatures of the self-heating reactions are due to the influence of the state of charge on the thermal stability of the electroactive materials, where highly delithiated electroactive materials become more reactive [12,13]. At 50%, 75%, 100% and 120% SOCs, self-heating reactions were followed by a thermal runaway behavior.

Fig. 3 shows the thermal behavior of the LMO-Graphite cell during the ARC measurements at 0%, 25%, 50%, 75%, 100% and 120% SOCs. As in the case of LCO-Graphite cells, a temperature drop is observed at some SOCs. Table 2 shows the onset temperatures of self-heating and thermal runway reactions of LMO-Graphite cell at different SOCs. At 0% SOC, self-heating and thermal runaway reactions are not observed. Self-heating reactions were followed by a thermal runaway behavior at 75%, 100% and 120% SOCs.

By comparing the thermal behaviors of LCO-Graphite and LMO-Graphite cells, some differences in the onset temperatures of self-heating and thermal runaway reactions are noticed. These

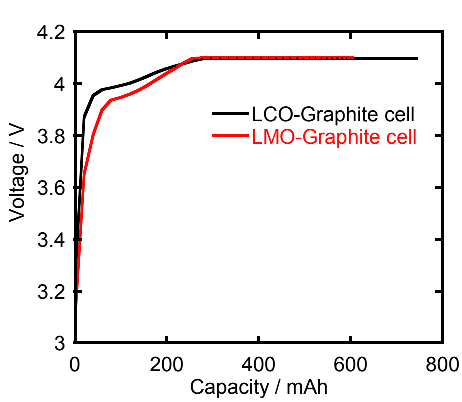

Fig. 1. Charging curves of LCO-Graphite and LMO-Graphite cells.

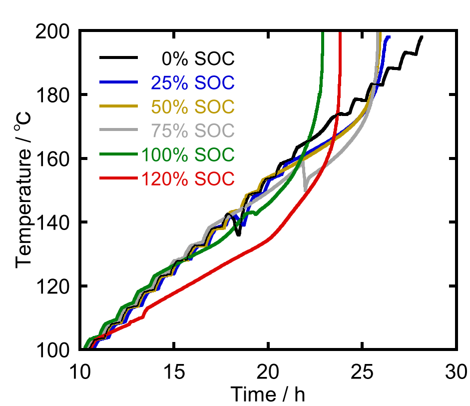

Fig. 2. ARC measurements of LCO-Graphite cell at 0%, 25%, 50%, 75%, 100% and 120% SOC.